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FACTORS AFFECTING THE LONG-TERM RESPONSE OF SURFACE WATERS TO ACIDIC DEPOSITION: STATE-OF-THE-SCIENCE

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Recent intensive study of the causes of surface water acidification has led to numerous hypothesized controlling mechanisms. Among these are the salt-effect reduction of alkalinity, the base cation buffering and sulfate adsorption capacities of soils, availability of weatherable minerals, depth of till, macropore flow, and type of forest cover. Correlative and predictive models have been developed to show the relationships(if any) between the hypothesized controlling mechanisms and surface water acidity, and to suggest under what conditions additional surface waters might become acid.
The US EPA is interested in surveying watershed characteristics to correlate with predictive model simulations in and effort to assess how many surface waters will become acid within certain timeframes. This document (Part A) is a review of our current knowledge of factors and processes controlling soil and surface water acidification, as well as an assessment of the adequacy of that knowledge for making predictions of future acidification. Section 2 is a data extensive, conceptual overview of how watersheds function. Section 3 is a closer look at the theory and evidence for the key hypotheses. Section 4 is a review of existing methods of assessing system response to acidic deposition.

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Chapter 1

INTRODUCTION

by

Robert S. Turner

1.0 INTRODUCTION

Recent intensive study of the causes of surface water acidification has led to numerous hypothesized controlling mechanisms. Among these are the salt-effect reduction of alkalinity, the base cation buffering and sulfate adsorption capacities of soils, availability of weatherable minerals (weathering rates), depth of till, macropore flow, and type of forest cover. Correlative and predictive models have been developed to show the relationships (if any) between the hypothesized controlling mechanisms and surface water acidity, and to suggest under what conditions additional surface waters might become acid. The U.S. Environmental Protection Agency (EPA) is interested in surveying watershed characteristics to correlate with predictive model simulations in an effort to assess how many surface waters will become acid within certain timeframes. This document (Part A) is a review of our current knowledge of factors and processes controlling soil and surface water acidification, as well as an assessment of the adequacy of that knowledge for making predictions of future acidification. Section 2 is a data extensive, conceptual overview of how watersheds function. Section 3 is a closer look at the theory and evidence for the key hypotheses. Section 4 is a review of existing methods of assessing system response to acidic deposition.

Chapter 2

An Overview of the Factors/Processes Controlling Surface Water Acidification

by

Robert S. Turner

2.0 AN OVERVIEW OF THE FACTORS/PROCESSES CONTROLLING SURFACE WATER ACIDIFICATION

2.1 DEFINITION OF TERMS

The Panel on Processes of Lake Acidification (PPLA), assembled by the National Research Council at the request of EPA, defined the acidification of lakes and streams (surface waters) as a decrease in alkalinity over time. They defined soil acidification as a decrease in the percent base saturation over time (PPLA, 1984). Alkalinity is defined as the concentration (in equivalents) of (CO_3^{2-}) plus (HCO_3^-) plus (OH^-) minus the concentration of (H^+) in solution (Stumm and Morgan, 1981). In eastern United States surface waters alkalinity generally is expressed as the concentration of bicarbonate anion (HCO_3^-) in microequivalents per liter (ueq/l) of water and is an index of the acid neutralizing capacity of the water. Waters with less than 200 ueq/l alkalinity are generally considered potentially sensitive to acidification. The percent base saturation of a soil is the concentration (in equivalents) of exchangeable base cations $(Ca^{2+}$, Mg^{2+}, K^+, $Na^+)$ divided by the total of exchangeable cations, or cation exchange capacity. Forest soils in humid regions often are naturally acidic; that is, they have low percent base saturation, with more exchangeable Al^{n+} and H^+ than base cations. For reasons described below, drainage through acidic forest soils does not necessarily result in acidic surface waters; nor does acidification of surface waters necessarily require acidification of soils.

2.2 HYPOTHESIZED CONTROLS ON SOIL AND WATER ACIDIFICATION

In conceptualizing how and at what rate soils and surface waters may become acidified it is useful to follow the flow paths of water and associated materials through different watersheds and observe what biogeochemical processes occur along the way. By comparing the outcome in watersheds that have little atmospheric input of strong mineral acids with watersheds that have high inputs of strong acids, we may be able to infer the relative rates of acidification by natural and anthropogenic acids. By comparing the outcome in watersheds with similar acid loadings but different hydrologic and biogeochemical characteristics, we may be able to infer the relative sensitivity to acidification of watersheds with different natural characteristics. The following sections summarize hypothesized controls on acidification as water passes into and through the watershed.

2.2.1 Inputs

The amount of precipitation and concentrations of dissolved ions received by a watershed influence the chemistry of water flowing through that system. In addition, dry deposition of materials in the form of soluble particles and gases affect the water chemistry. Climate, the physiography of the area (elevation, slope, aspect), the nature of the vegetation cover, and the location of the watershed relative to point and regional sources of airborne materials will determine in what forms the materials will be deposited (wet, dry, gaseous, fog, snow), the total loading of materials to the watershed, the seasonal distribution of material loading, and the intensity of events. The total amount of precipitation, concentrations of dissolved ions such as H^+, NH_4^+, Mg^{2+}, Ca^{2+}, K^+, Na^+, SO_4^{2-}, NO_3^-, Cl^-, and HCO_3^-, plus concentrations of airborne particles and gases, each vary differently with the physiographic, climatic, and location variables. The controls on atmospheric material inputs to watersheds are indeed complex and poorly understood, and the actual inputs are difficult to measure.

Nevertheless, regional patterns in material deposition have been measured and mapped (e.g., U.S. EPA 1984, NADP in press), showing wet precipitation inputs of H^+, NH_4^+, base cations, and strong acid anions. These data may be useful in making regional assessments of the potential for changes in surface water chemistry. However, it must be recognized in making predictions for individual watersheds, that local elevation, aspect, slope, and material sources may radically alter the yearly water budgets and chemical inputs from the regional norm, and that no similar regional data on dry deposition exists.

2.2.2 Canopy-Atmosphere Interactions

The extent to which a forest canopy will accelerate or delay watershed acidification depends on the importance of two processes mediated by the canopy: (1) input of additional amounts of airborne materials to the watershed (by dry deposition and fog or cloud water) due to interception by the large surface area of the canopy, and (2) alteration of water chemistry as it passes through the canopy.

The first of these processes is dependent on physical and physiological characteristics of the canopy. Leaf surface area, surface texture, and stomata location and function, along with canopy shape and percent evergreen cover, interact with meteorologic parameters such as wind speed, turbulence, relative humidity, thermal stability, and timing of precipitation events to control the rate and amount of particle and gas dry deposition. The study of these interactions and differences between canopy types is in its infancy, but comparisons of throughfall under deciduous and coniferous canopies suggest greater interception of particles, gasses, and fogs by coniferous forests (Mayer and Ulrich, 1982; Lindberg _et al_., 1984). We cannot, at present, quantify relationships among species, leaf area, and increased deposition on a stand, watershed, or regional level.

Complicating the assessment of additional material inputs to the watershed is the fact that canopies alter the chemistry of water passing through them. This alteration involves ion exchange, chemical reactions, and both passive and active uptake of deposited materials from atmospheric sources and from sources within the watershed. Trees cycle materials from the soil to the canopy where they can be transformed, exchanged, leached, or metabolized. Trees also transform materials sorbed through leaf surfaces or taken in through stomata and translocate them to storage sites within the tree or retain them for later leaching. Thus, the difference between the chemistry of incident precipitation and throughfall plus stemflow is due to a complex mixture and interaction of materials deposited from the atmosphere and materials cycled by the tree from the soil.

A net increase or decrease in alkalinity of incoming precipitation may occur in the canopy, but many factors determine whether this represents a net change in alkalinity for the watershed as a whole. For example, deciduous canopies in most locations appear to neutralize incoming precipitation to some extent. This may result from exchange of H^+ for base cations (e.g., K^+) in the canopy, which may require the tree to take up additional base cations through the roots, releasing H^+ to the soil in the process, or it may result from protonation of a foliar weak base produced by photosynthesis (e.g., HCO_3^- or an organic anion), thereby reducing the alkalinity of the solution. Thus, the apparent canopy neutralization may or may not result in less net watershed acidification. (See also discussion of cation redistribution in Sections 2.2.3 and 3.5 below.)

Can canopy type significantly affect the rate of watershed acidification? Results published to date seem to indicate that coniferous canopies intercept more acidic materials than deciduous canopies due to greater leaf area and year-round retention of foliage. It is not clear, however, to what extent observed differences in throughfall beneath coniferous and deciduous forests are due to differences in canopy interception versus differences in elemental cycling by different tree species. The canopy interactions-dry deposition question remains an open one. We cannot, at this point, quantify a difference in rates of watershed acidification due to canopy-atmosphere interactions.

2.2.3 Soil Interactions

2.2.3.1 Hydrologic Pathways

Numerous biogeochemical processes occurring in soils may add alkalinity to the water or may acidify the water passing through them. However, the extent to which these processes contribute to the chemistry of surface water depends on the pathways the water takes through the watershed. Water which falls directly on streams or lakes, of course, bypasses these reactions altogether, and lakes with high surface area to watershed area ratios may be rapidly acidified by acidic deposition. In most watersheds, however, the bulk of the water flows over or through soils before entering surface waters.

The chemical characteristics of the soils through which most water flows will affect the chemistry of the water that reaches surface waters. For example, a watershed with numerous bedrock outcrops and thin soils may have flashy surface water flows with a chemistry that reflects only limited contact or interaction time with those soils. A watershed with deep, permeable soils might have more continuous flows and water chemistry indicating that numerous reactions have occurred since the water left the atmosphere. That same watershed, however, could exhibit very different chemistry if most water flows out of it during spring snowmelt, when soils are saturated and the bulk of the water flows over the surface or through only the shallow soils. Likewise, a deep soil with a shallow restrictive layer such as a clay horizon or hardpan could produce surface water with a very different chemistry than would be predicted from the characteristics of the deep soils.

Identifying hydrologic pathways and quantifying flow rates through watersheds is a young and presently very dynamic field of study. Several modeling approaches and field experiments are being tested. Although the conceptual relationships between water transport, season, watershed physiography, and soil depth and texture are fairly clear, a validated model that is transferable to other types of watersheds does not yet exist.

2.2.3.2 Cation Leaching and the Salt Effect

Until recently the mechanism responsible for acidification of surface waters was thought to require the prior acidification of watershed soils through replacement of base cations by H^+ (cation exchange buffering) and subsequent leaching of base cations and protolytic cations (e.g., H^+, Al^{3+}) in association with the strong acid anions. Soil scientists argued that this soil acidification was not possible given the current levels of acidic inputs and the immense buffering capacity of the soil, yet aquatic scientists insisted surface waters were being acidified. The apparent conflict was resolved when it was recognized that in acid soils, the increased strong acid anion concentration can depress the alkalinity of the solution via the salt effect (Seip, 1980; Reuss and Johnson, 1985). The salt effect describes the phenomenon whereby H^+ and Al^{3+} concentrations in soil solution increase in response to an increase in total mineral acid anion concentration. This alkalinity depression may be accompanied by little reduction in soil solution pH due to cation exchange in the soil, but may result in a major reduction in surface water pH. Because soil CO_2 pressures are greater than atmospheric CO_2 pressure, soil water that has some alkalinity degasses CO_2 when it emerges into surface waters, and pH rises. Soil water that has zero or negative alkalinity does not experience a pH rise upon degassing when it reaches atmospheric pCO_2 conditions, and remains near the pH it was in the soil. Higher Al^{3+} mobility and surface water acidification result.

Although the salt effect and base cation leaching mechanisms are not mutually exclusive, the fundamental differences between them form one hypothesized basis for the categorization of watersheds into those which respond immediately to acidic deposition (salt effect), and those which respond only after some delay (base cation leaching). Both mechanisms are inherent in several of the current models that describe the chemical effects of acidic deposition on soil and water chemistry (Reuss, 1980; Christophersen et al., 1982; Chen et al., 1983; Reuss, 1983; Reuss and Johnson, 1985). (See Section 3.4 for further discussion of the theory and data requirements of the cation exchange and salt effect mechanisms.)

2.2.3.3 Anion Mobility

Several factors control the magnitude of the salt effect and rate of cation leaching. Most important among these is the concentration of anions in solution. All humid-region soils will acidify naturally over time, due to leaching of base cations in association with HCO_3^- and organic anions that are produced naturally in the soil. This natural soil acidification is self limiting, however, because these anions protonate to form weak acids that will not dissociate at low pH. Addition of strong acid anions in acidic deposition, however, allows the cation leaching/soil acidification process to continue unchecked if anions are mobile and causes the salt-effect alkalinity depression that acidifies surface waters. Controls on anion mobility thus are critical in determining how rapidly surface waters and soils will acidify.

The major anion in acidic deposition is sulfate (SO_4^{2-}), and most scientific and policy attention has been devoted to it. Soils adsorb SO_4^{2-} according to a concentration-dependent function; that is, a given soil will continue sorbing SO_4^{2-} until the concentration of adsorbed SO_4^{2-} reaches an equilibrium with SO_4^{2-} in solution. Sulfate concentration in output solution will increase as the concentration of sorbed SO_4^{2-} increases, at a rate that depends on SO_4^{2-} loading, not solely on input SO_4^{2-} concentration. In some soils the equilibrium, or ratio of adsorbed SO_4^{2-} to SO_4^{2-} in solution, is much higher than others (i.e., some soils have higher sulfate adsorption capacities than others). These soils will sorb SO_4^{2-} for a longer time before the equilibrium is reached, thus retarding the rate of increased SO_4^{2-} concentration in soil solution and associated cation leaching or salt-effect alkalinity depression. SO_4^{2-} adsorption capacity is thought to be positively correlated with free iron and aluminum oxides in soil and inversely correlated with organic matter content of the soil (Johnson and Todd, 1983), though Singh (1984a,b,c,d) has shown that the situation may be more complex. These characteristics vary within soil profiles, surface soils having low SO_4^{2-} adsorption capacity and subsoils having higher capacity. These factors also vary between regions, the highly weathered soils of the Southeast generally having higher SO_4^{2-} adsorption capacity than soils of the Northeast.

Because the amount of SO_4^{2-} adsorbed is dependent on the concentration of SO_4^{2-} in solution, it also may be affected by hydrologic/climatic factors. For example, a watershed with high evapotranspiration (ET) and dry summers might adsorb all incoming SO_4^{2-} during that season due to high soil solution concentrations. In contrast, a wetter watershed with soils of the same SO42- adsorption capacity would not reach the same solution concentrations, and less SO_4^{2-} would be immobilized. To the extent that the SO_4^{2} sorbed by the former watershed does not desorb during a wetter season, that watershed would have a more delayed response than the latter. If the SO_4^{2} does desorb during the spring wet season, a strong acidic pulse could occur. This ET difference could occur, for example, between watersheds in the southeast (high ET) and the northeast (low ET), or between watersheds in the same region but with south-facing aspect (high ET) or north-facing aspect (low ET), all other factors being equal. Finally, the hydrologic pathway that water follows through a watershed may determine the amount of SO_4^{2-} adsorbed. Shallow throughflow of water primarily through low-adsorption-capacity surface soils could result in surface water acidification even though the deeper soils had high sorption capacity.

Sulfate adsorption capacity is another important hypothesized basis for the categorization of watersheds into ones that will respond quickly and ones that will exhibit a delayed response. Unfortunately, laboratory and field data on the SO_4^{2-} adsorption capacity of soil are very meager. The use of adsorption characteristics determined from laboratory columns as inputs to models is hazardous because we do not know the relationships between those characteristics in disturbed laboratory columns and in the field. (See Section 3.3 for further discussion of SO_4^{2-} adsorption.)

Nitrate (NO_3^-) is the other important strong acid anion in acidic deposition. In contrast to SO_4^{2-}, which enters watersheds in amounts greater than biological demands, most NO_3^- (and NH_4^+, which could be converted to NO_3^-) is efficiently incorporated into biomass in most watersheds. Recent evidence, however, suggests that some watersheds are not retaining NO_3^- (Todd et al., 1975; Martin, 1979). These appear to be watersheds with mature vegetation with a relatively low nitrogen requirement. More work is needed to determine the extent of forests/watersheds which release NO_3^-, the rate of increase of such areas as forests mature, whether the NO_3^- export is a seasonal phenomenon that occurs only when biological uptake is low or only along shallow hydrologic pathways, and whether the NO_3^- concentrations are high enough or will become high enough alone or in conjunction with SO_4^{2-} to cause substantial cation leaching or alkalinity depression via the salt effect.

2.2.3.4 Cation Withdrawal, Redistribution, and Replenishment

Other factors that affect cation leaching and the salt effect include cation withdrawal and redistribution within the soil profile by vegetation, and replenishment of cations to the exchange complex by atmospheric inputs and weathering of minerals within the soil profile. These factors do not directly affect the absolute amount of cation leaching, but control the distribution of individual ionic species and determine whether the soil will acidify or maintain an equilibrium between cations lost and cations resupplied by weathering of primary minerals. In effect, these factors, along with SO_4^{2-} adsorption, may determine how delayed a watershed's response will be.

Aggrading (growing) forests accumulate nutrients in their biomass each year, and also cycle larger quantities of nutrients from the soils, through their foliage, back to the soils (in throughfall and litterfall). The yearly accumulation results in a net acidification of the soil due to uptake of excess cations over anions, which the tree balances by exporting H^+ ions through the roots. This can result in acidification of some soils comparable to yearly leaching by acidic deposition (Alban, 1982; Johnson and Richter, 1984), and can result in permanent acidification if the trees are harvested from the site. The yearly cycling of nutrients or eventual death and decomposition of the trees on site returns the cations to the surface soil, resulting in no net acidification, but rather in a redistribution of nutrients within the soil profile. Thus, cation withdrawal and storage in vegetation may significantly accelerate acidification of some soils on the 10 to 100 year time scale that we are interested in. Yearly cycling and redistribution of cations to the surface soils controls the abundance of base cations in those soils, and retards acidification of the surface soils at the expense of deeper soils. Some information is available on nutrient distribution and cycling in major forest types, but little is known about changes in requirements or cycling as forests mature, about relationships with historic land management practices, about linkages with hydrologic pathways, or relationships to differing soil characteristics and climate. The variation in distribution and cycling of nutrients, between watersheds within a region or between regions for a given forest type, is unknown.

Net base cation replenishment to the soil exchange complex can occur through two processes: (1) inputs from the atmosphere, and (2) from mineral weathering. Both of these are straightforward in concept but extremely difficult to measure.

National Atmospheric Deposition Program (NADP) measurements provide an estimate of cations deposited in wet deposition, but do not include dry deposition which may be substantial for some elements, particularly base cations. Wet and dry deposition have industrial, terrestrial, and marine sources, and vary greatly with the origin of the airmass. NADP data can provide at least a minimum value of atmospheric input of cations to watersheds (given the caveats mentioned in Section 2.2.1). A survey of local sites that monitor wet and dry deposition might aid in obtaining better input numbers, but it must be remembered that no widely accepted methods exist for monitoring dry deposition to watersheds.

Measuring the rate of base cation resupply from mineral weathering is a more difficult problem. Direct measurements of weathering rates and resupply of base cations can only be accomplished over a long period of time by using mass-balance techniques in lysimeter-plot or watershed-level studies and direct measurement of the change in exchangeable cations in the soils at the beginning and end of the time interval. Even this technique has wide margins of error due to uncertainties in quantifying wet-dry inputs, flux of water past the lysimeter or out of the watershed in stream and groundwater, uptake by vegetation, and a probable small change in exchangeable cations measured as the difference between two large numbers with high variance.

Other techniques that could be used to estimate mineral weathering include: (1) measurement of weathering products such as silica or chloride in the surface waters from which weathering rates may be calculated, knowing the mineral types and abundance in the watershed; (2) study of mineral grain etching, weathering rinds (secondary minerals that form on the surface of primary mineral grains as they weather), and mineral abundance in the watershed to calculate weathering rates; and (3) laboratory studies of mineral weathering extrapolated to the field. The first of these might be the easiest to accomplish on a survey basis. Its biggest problem is that the element to be measured in the field must not undergo biologic uptake or be involved in cation exchange, soil adsorption, or secondary mineral formation in either the terrestrial system or surface waters. Also, it must have zero or well-known atmospheric input. Few or no commonly measured ions meet these requirements, so an unknown amount of uncertainty is added to the calculation. Calculating a rate from a surface water measurement also does not tell you where the weathering occurred, e.g., within the rooting zone (where it could replenish the exchange complex) or deep within the till or regolith. Only a knowledge of the relative contributions of different hydrologic pathways and distribution of the mineral types could help locate the weathering zone.

Study of mineral grain etching and weathering rinds could show important weathering differences within a soil profile and between watersheds that have similar mineralogy but different aspect, hydrologic pathways, and vegetation types, for example. It could be used alone or in conjunction with the method above, but is very labor intensive and involves some gross estimates and assumptions. It would be very difficult or impossible to discern any recent increase in cation resupply rates using this method, because the technique analyzes mineral alterations that occur over thousands of years or longer.

The last technique, of measuring weathering rates under controlled laboratory conditions, is useful as a comparative tool to test relative weatherability of different soils. However, a measurement of abrasion pH (pH measured on fresh, finely ground soil) might give as good an index. With neither of these techniques is it known how the results relate to field conditions. A soil core, even if taken to the laboratory with a minimum of disturbance, will have altered input rates, water content, CO_2 content, temperature, and a multitude of biotic processes. These factors are all critical determinants of weathering rates, and the results of such studies are difficult to interpret in the context of assessing resupply of base cations to exchange sites or the length of delayed response a watershed might exhibit.

To summarize, an easy, inexpensive, sure technique of measuring weathering/cation resupply rates, and differences between watersheds within a region, does not exist. Some generalizations and assumptions could be made using lake survey data and soil minerals sampled from every watershed to develop a rough estimate of weathering rates and differences between watersheds. The uncertainty of measurement would be very high, however, and likely would not help distinguish between watershed response delays of 10 or 100 years. (Our knowledge of cation withdrawal, redistribution, and replenishment is discussed in greater detail in Sections 3.5 and 3.6.)

2.2.4 In-Stream and In-Lake Processes

Streams and lakes are both (1) receptors of dissolved and particulate materials transported from the surrounding watershed and deposited directly from the atmosphere, and (2) biogeochemical reactors that further transform these materials. An assessment of the characteristics that control whether a lake will respond to acidic deposition immediately or with a delay thus must include not only a determination of controls on fluxes of alkalinity, acidity, and associated cations and anions from the terrestrial to the aquatic system, but also internal hydrologic and biogeochemical processes that mediate the concentrations, transformations, and fluxes of these materials within the surface waters.

Spatial and temporal variability of inputs to, and mixing of, streams and lakes influences the flux of materials and extent of reactions that can take place. Geochemical (e.g., cation exchange, weathering, SO_4^{2-} adsorption) and biological processes (e.g., nitrate and sulfate reduction, primary productivity) within the sediments and water column generate alkalinity and acidity. The acidification of the waters may influence the rates at which these internal processes take place, with positive and negative feedbacks possible. Enough is known about these processes for several lakes to know that they are important in making the direct/delayed assessment (e.g., Hongve, 1978; Cook and Schindler, 1983; Kelly _et al_., 1982; Wright, 1983; Goldstein and Gherini, 1984), and at least one of the current models incorporates in-lake processes in its projections (Chen _et al_., 1983). The project needs to be designed to collect and incorporate the appropriate lake data in addition to the terrestrial ecosystem data.

2.3 WATERSHED CLASSIFICATION

2.3.1 Continuum of Response, and Direct/Delayed/Capacity Protected Categories

Due to the multiple hypothesized mechanisms (and possibly also some unrecognized ones), and due to the great variability of watershed characteristics within the eastern United States, it is reasonable to expect that there will be a continuum of response of lakes to continued acidic deposition. Galloway et al. (1983) proposed a seven-step conceptual framework for understanding surface-water acidification and identifying research needs. Reuss (1984, unpublished) added the salt-effect mechanism to that framework [based on the concepts published in Reuss and Johnson (1985)], to produce the conceptual framework of three different watershed types shown in Figure A.2.1 and discussed below. These concepts and the related knowledge of the members of the National Research Council PPLA resulted in their simplified conceptual categorization of lake watershed acidification into quick (direct) response (on the order of a few years to 20 years), delayed response (on the order of decades or longer), and capacity protected/no response (centuries or millennia) (PPLA, 1984).

Figure A.2.1 shows the sequence of hypothesized changes in surface water alkalinity and pH based on differences in soil acidity (base saturation) and SO_4^{2-} adsorption capacity.

Step 1. Surface water quality is at steady state, with a dynamic equilibrium established between atmospheric inputs of water and dissolved constituents, weathering, and biological transformations and cycling of nutrient and nonnutrient elements.

Step 2. An increase in solution concentration due to an increase in strong acid anions causes depression of alkalinity and pH (salt effect).

The magnitude of the response (alkalinity and pH depression) is dependent on the initial alkalinity of the solution, on the base saturation of the soil or sediment, and on the cation exchange selectivity of the soil or sediment. [High-base-saturation exchangers have relatively little exchangeable H^+ to give up to solution. Total cation exchange capacity (CEC) is not a factor in this step.]

The rate of the response is dependent on rate of increase of strong acid anion concentration in solution. This increase is in turn dependent on hydrologic, geochemical, and biological conditions discussed in Sections 2.2.3 and 2.2.4. The amount of SO_4^{2-} adsorption will determine the time delay in this step.

With solution alkalinity substantially greater than zero (e.g., > 100 ueq/L), the soil solution pH will be depressed only slightly below normal soil CO_2 equilibrium pH, and stream or lake water pH will rapidly rise to atmospheric CO_2 equilibrium level as zero, soil solution pH will still be depressed only slightly below normal due to cation exchange of most H^+ ions, but stream or lake water pH will remain low, since there is no alkalinity in the water to react with H^+ and degas as CO_2 as the soil water is discharged to the surface water environment. This critical relationship is discussed further in Sections 3.2.3 and 3.4.

Step 3. Acidification of soil, soil solution, sediments, and surface water occurs due to depletion of base cations leached in association with mobile anions.

The extent of acidification due to depletion of base cations is limited by cation selectivity of exchange sites. At low base saturation, base cations are

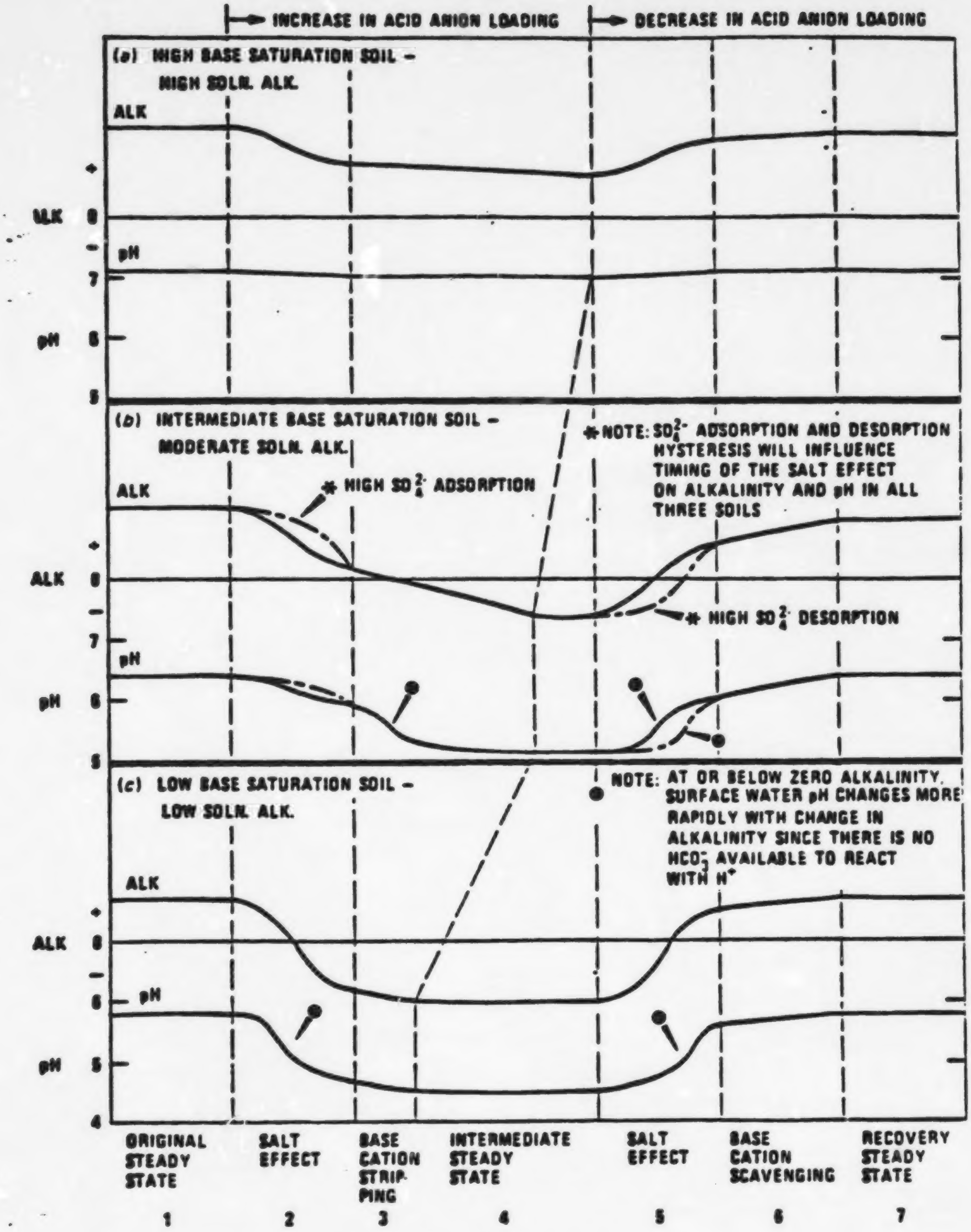
INCREASE IN ACID ANION LOADING
DECREASE IN ACID ANION LOADING
(a) HIGH BASE SATURATION SOIL – HIGH SOLN. ALK.
ALK
+
ALK 0
–
pH
7
pH 6
5
(b) INTERMEDIATE BASE SATURATION SOIL – MODERATE SOLN. ALK.
* HIGH SO_4^{2-} ADSORPTION
* NOTE: SO_4^{2-} ADSORPTION AND DESORPTION HYSTERESIS WILL INFLUENCE TIMING OF THE SALT EFFECT ON ALKALINITY AND pH IN ALL THREE SOILS
ALK
+
ALK 0
–
7
* HIGH SO_4^{2-} DESORPTION
pH
pH 6
5
(c) LOW BASE SATURATION SOIL – LOW SOLN. ALK.
● NOTE: AT OR BELOW ZERO ALKALINITY, SURFACE WATER pH CHANGES MORE RAPIDLY WITH CHANGE IN ALKALINITY SINCE THERE IS NO HCO_3^- AVAILABLE TO REACT WITH H^+
ALK
+
ALK 0
–
6
pH
pH 5
4
ORIGINAL STEADY STATE
SALT EFFECT
BASE CATION STRIPPING
INTERMEDIATE STEADY STATE
SALT EFFECT
BASE CATION SCAVENGING
RECOVERY STEADY STATE
1
2
3
4
5
6
7

Figure A.2.1. Hypothesized steps in surface water alkalinity and pH response to an increase and then a decrease in strong acid anion loading to (a) a "capacity-protected" watershed, (b) a "delayed-response" watershed, and (c) a "direct-response" watershed.

held very tightly on exchange sites, and H^+ and Al^{3+} become the dominant cations accompanying mobile anions in solution.

The timing and rate of base cation depletion depends on the SO_4^{2-} adsorption capacity of the soil or sediment, solution SO_4^{2-} and NO_3^- concentrations, base saturation, and CEC of the soil or sediment. Weathering of primary minerals may keep up with, or reduce the rate of, base cation depletion from exchange sites. Factors controlling the rates of these component biogeochemical processes are discussed in Sections 2.2.3 and 3.2.

Alkalinity and CO_2 partial pressure of soil and surface waters will affect solution pH as in Step 2 above.

Step 4. A new steady state is established and maintained when atmospheric inputs, hydrologic processes, and biogeochemical reactions again reach equilibrium. This occurs if weathering of primary minerals in young or very deep soils with abundant weatherable minerals or dissolution of secondary silicate clays or sesquioxides in more mature soils keeps pace with strong acid anion inputs. The point at which this steady state is reached is the same as the endpoint of base cation depletion in Step 3 above, and thus depends on the same component processes discussed in Sections 2.2.3 and 3.2. If the equilibrium established is due to primary mineral weathering, solutions will be dominated by base cations, whereas if it is due to secondary mineral weathering, solutions will be dominated by H^+ and Al^{3+} ions.

Steps 5, 6, and 7. Upon reduction of strong acid anion input to the system, recovery to the original equilibrium conditions is a reversible process. The extent of recovery is not limited, given enough time. The rate of return of pH and alkalinity to original levels is controlled by delayed release of SO_4^{2-} from sorption sites and by rates of weathering or other base cation inputs into the system. A fundamental difference between recovery due to the salt effect and recovery by means of the cation scavenging process exists in the rate at which each occurs. In soils that do not retain sulfate or in soils where sulfate is irreversibly retained, alkalinity and pH depression due to the salt effect will be removed immediately upon reduction in strong acid anion loading (SO_4^{2-}, NO_3^-, Cl^-). If this results in a shift from negative to positive alkalinity, the pH shift may be quite substantial. Recovery from acidification due to cation leaching may require decades or much longer.

Note that factors discussed in Section 2.2 such as variations in physiography, canopy types, hydrologic pathways, vegetation withdrawal and redistribution, and in-stream and in-lake processes are not explicitly included in this conceptual framework. For purposes of simplicity, these factors are assumed to be equal for each type of watershed described. In the real world they might all influence the extent of alkalinity depression or rate of acidification (length of delay), and must be factored into any model and regional assessment along with the soil equilibrium relationships.

2.3.2 Supporting Evidence

The evidence on which this conceptual framework was built exists in both relatively long-term, ecosystem-level data collected at a few sites such as Hubbard Brook, New Hampshire, Coweeta, North Carolina, and Walker Branch, Tennessee, as well as in more-limited and shorter-term data that have been collected at numerous additional sites shown in Figure A.2.2. Results of studies conducted at these sites are scattered widely through the peer-reviewed literature. The participants on the Panel on Processes of Lake Acidification mentally synthesized much of these data during their formulation of the direct/delayed/no response categories. Within the scope of this document only broad generalizations can be drawn from the available results. Clearly, though, support for a regional assessment project based on this conceptualization should include a compilation and critical review of existing data sets and conclusions, as well as generation of new data sets, for testing/refining the conceptual framework.

Regional patterns that have emerged can be divided into patterns of surface water chemistry (e.g., Omernik and Powers, 1983) and patterns of geology and soil chemistry (Olson _et al._, 1982; McFee, 1980; Norton, 1980). Acidic streams and lakes occur mainly in the northeastern United States. Very few acidic lakes occur in the Southeast, but very few small, natural lakes occur at all in the Southeast. Low-order southeastern streams also are not generally as acidic as northeastern streams, and they generally contain lower SO_4^{2-} concentrations. Many high-elevation, low-order southeastern streams do have alkalinity as low as their northeastern counterparts, however, and this is cause for concern about future acidification of these streams that are important for sport fishing. Smith and Alexander (1983) reported data from U.S. Geological Survey (USGS) benchmark sampling stations supporting these generalizations. They also reported trends showing a decrease in SO_4^{2-} concentrations from northeastern stations and an increase in SO concentrations in southeastern streams, and related these trends to similar trends in SO_2 emissions in surrounding states. Unfortunately, recent critical analyses of existing surface water data show that there is very little reliable data available for assessing historic changes in surface waters due to acidic deposition or other causes (Kramer and Tessier, 1982; Hendrey _et al._, 1984). The National Surface Water Survey will provide the first consistent database of existing conditions.

Differences between three lake watersheds within a small region have been intensively studied in the ILWAS project, and studies of 20 additional water-

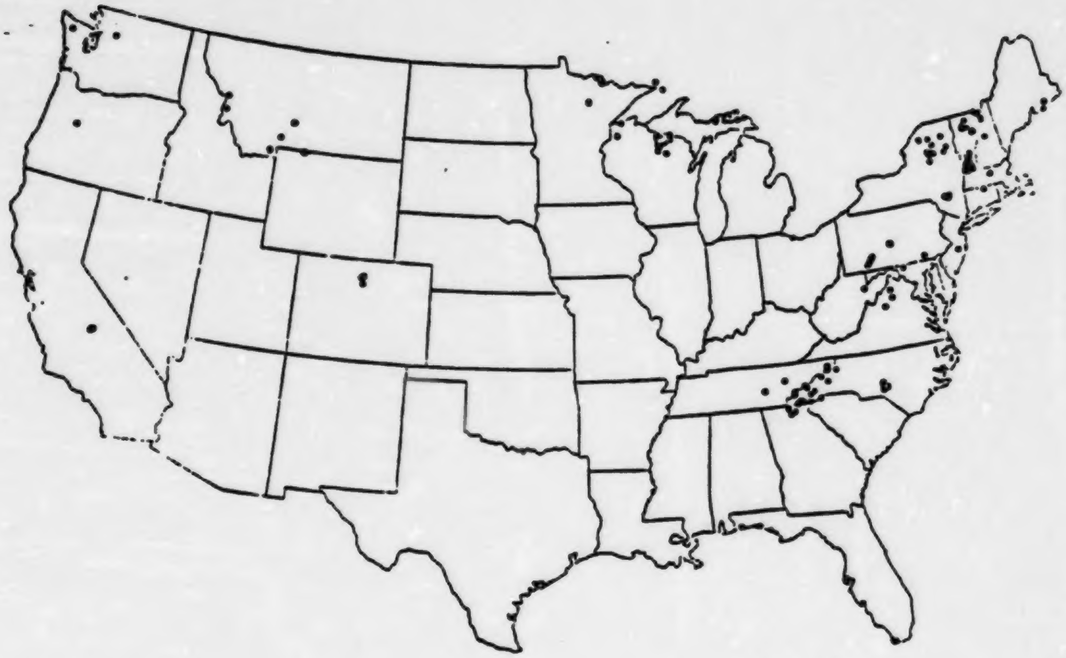

Figure A.2.2. Network of long-term monitoring and intensive terrestrial/ aquatic study sites.

sheds are continuing with the RILWAS project, sponsored by the Electric Power Research Institute. These projects are integrative studies utilizing intensive field data gathering and watershed monitoring, along with a sophisticated modeling effort. The results are voluminous (Chen et al.m 1983; Murdoch et al., 1984; Galloway et al., 1984; Goldstein and Gherini, 1984), and suggest that the processes most important to controlling lake chemistry at those sites are shallow flowpaths through relatively unreactive soils in one watershed and deeper flow through weatherable till in a second watershed. The third lake watershed was too large to distinguish the controlling factors even with intensive study. Shallow-soil chemical characteristics were essentially identical between the watersheds. In-lake processes were also found to be important.

Soil properties thought to control surface water acidification also show regional patterns. Some of these are shown for the eastern United States in Figures A.2.3-6, drawn from the Geoecology Data Base (Olson et al., 1980; Olson et al., 1982). The most critical property, base saturation (Figure A.2.3), is low throughout the Southeast and in high-elevation and sandy outwash soils of New England. These are naturally acidic soils in which the salt effect could be significant if anion concentrations become high enough. Cation exchange capacity (CEC) and exchangeable bases (Figures A.2.4-5) are low throughout the Southeast, but significantly higher in most of the Northeast. Watersheds with low CEC and low exchangeable base soils might acidify immediately due to the salt effect (direct response), or exhibit a less delayed response than those with higher CEC and exchangeable bases. Sulfate adsorption capacity, related to iron and aluminum oxides and inversely related to soil organic matter content, is thought to be high in Ultisols, which occur in the Southeast and middle Atlantic states, and low in Spodosols, which occur primarily in the

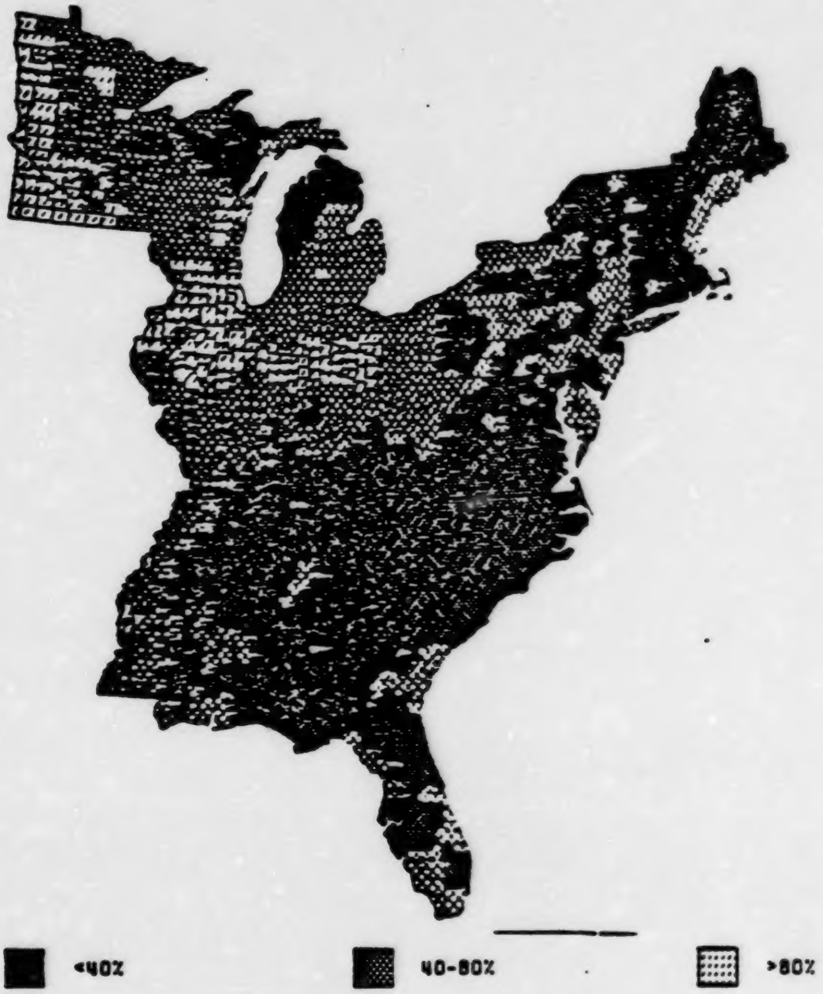

Figure A.2.3. Average county surface-soil base saturation levels.

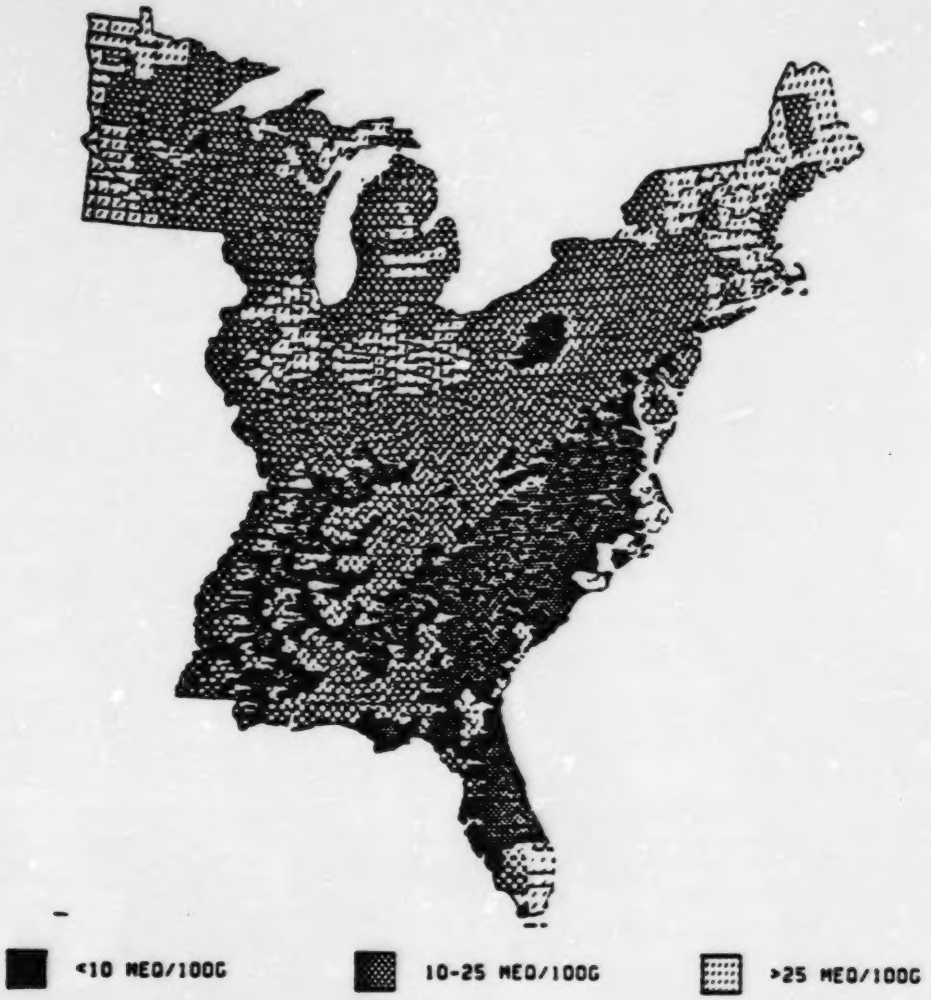

Figure A.2.4. Average county surface-soil cation exchange capacity.

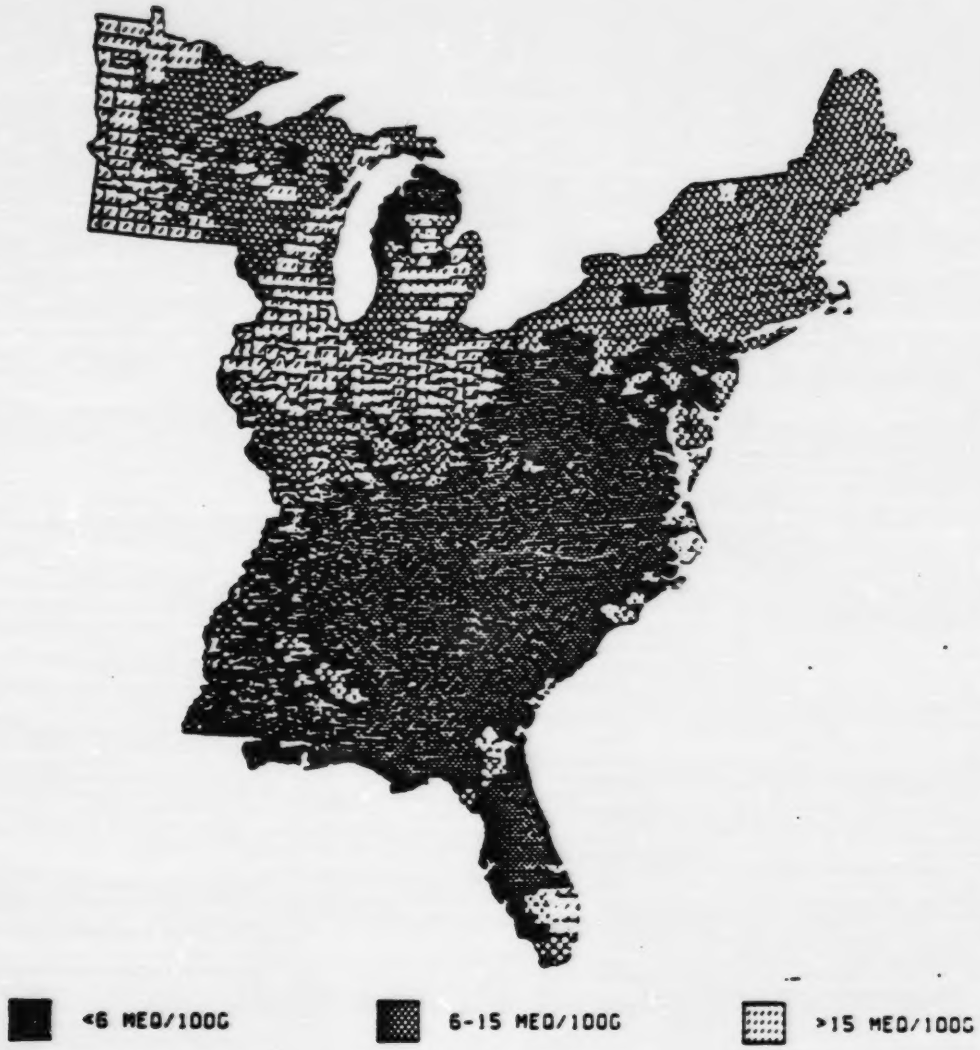

Figure A.2.5. Average county surface-soil exchangeable base levels.

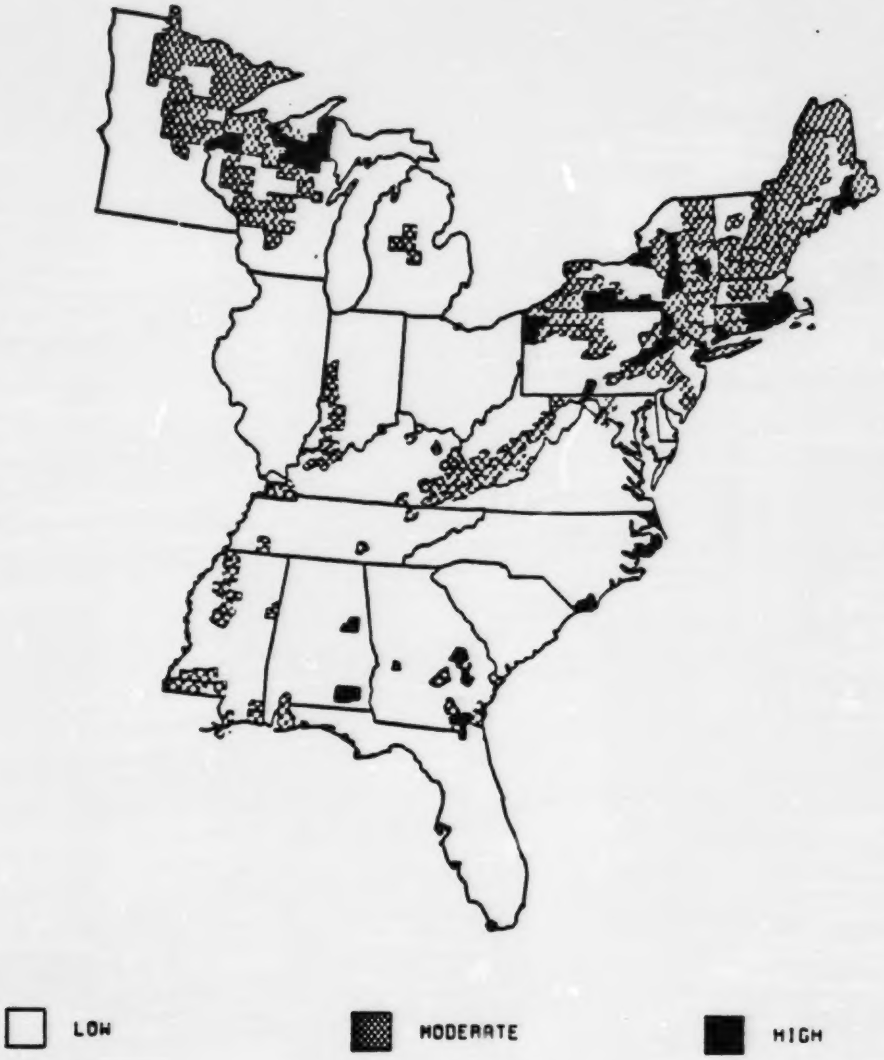

Figure A.2.6. Areas with potential to transfer acid to aquatic systems based on county-level average base saturation, sulfate adsorption capacity, and bedrock sensitivity. High = direct response, Moderate = delayed response, Low = capacity-protected or more delayed response.

Adirondacks, New Hampshire, and Maine. Inceptisols, which occur throughout southern New England and on the ridges of the middle Atlantic and southeastern states, may have high or low SO_4^{2-} adsorption capacity. Figure A.2.6 shows areas that might be predicted to have direct, delayed, and capacity protected watersheds based on base saturation, sulfate adsorption capacity, and bedrock sensitivity. Criteria for each category were based on Seip (1980) and are listed in Olson et al. (1982).

Although the above analysis does show regional patterns and differences between counties within a region, it is unsuitable for providing input data to models for predicting behavior of watersheds within those regions. The data are generalized to averages for all forested soils within each county, thereby masking any sensitive areas within counties that are otherwise largely insensitive. These base saturation and CEC data are determined at a buffered pH using standard Soil Conservation Service (SCS) procedures, and these values are very different from values determined at field pH of the soils. The field pH values are needed as input to the predictive models. Finally, the SO_4^{2-} adsorption capacity of most soils is unknown, and such a gross generalization based on soil order is too uncertain for analysis of differences in delay within regions. All caveats aside, it will be interesting to overlay lake survey results with these maps to test the credibility of this analysis which was performed long before the direct/delayed/capacity protected concept was developed.

2.3.3 Seasonality

An apparent problem with the grouping of watersheds into direct/delayed/capacity protected categories (which imply at least some sense of stability over time) is that some watersheds show seasonal acidification or episodic acidification due to major storm events (e.g., Panther Lake in the Adirondacks or Raven Fork in the Smoky Mountains). These watersheds during most times of the year have circumneutral waters due to soil or other characteristics typical of delayed response or capacity-protected watersheds. However, the acidic pulses associated with snowmelt or storms may regulate the biotic community of the surface waters. An assessment of waters at risk needs to recognize and attempt to quantify such cases, which may not clearly fit into the general categorization scheme.

2.3.4 Regional Assessment of Direct/Delayed/Capacity Protected Categories

Policymakers require information concerning how many lakes/watersheds in a region are likely to become acidic within a certain timeframe, so that they can evaluate costs and benefits of alternative control strategies (or no action). An approach such as that used by Olson *et al*. (1982), described in Section 2.3.2 above, could be used to categorize areas into three response categories using predictive models driven by the area-average values for hypothesized critical environmental factors. It would then be necessary to assume all (or some distribution of) lakes in each area respond as predicted and aggregate the number of lakes in each area by response category into regions to give the total number of lakes in each response catagory in each region. An alternative approach would be to identify a random sample set of lakes within a region, characterize each lake watershed according to the hypothesized critical environmental factors, determine the response category of each lake watershed by modeling based on the watershed characterization, then scale back up to the region to get a statistical estimate of number of lake watersheds in each category.

The first approach is useful if homogeneous areas can be identified in which all lakes would be expected to respond the same way. Counties clearly are not the appropriate unit (but they do represent a relatively small mapping unit on a regional scale whose boundaries exist in digitized form and for which a large database of environmental factors exists). A mapping unit based on the combination/integration of several natural boundaries such as geologic contacts, physiographic units, soil series, soil associations, or other soil taxonomic groupings, and/or vegetative cover would be more appropriate.

The second approach requires a relatively large random sample set of lakes to adequately represent the many combinations of hypothesized critical environmental factors. It also requires an intensive sampling scheme at each watershed to adequately characterize each.

Because, based on our current knowledge and resources, we cannot identify a homogeneous mapping unit that fits our needs, yet we can identify enough natural pattern to make a purely statistical design unnecessary, some combination of the two approaches seems optimal. Natural regions that have been identified, such as alkalinity regions, major land resource areas (MLRAs), or soil taxonomic groupings, could be characterized in terms of response category based on hypothesized mechanisms. A stratified random sampling of individual watersheds within each region would be made, or a random sample drawn from all lake watersheds could be taken. Each watershed would be mapped according to soil characteristics and vegetative cover, followed by hydrologic, chemical, and biological characterization of each mapping unit. Sampling of watersheds would be designed to characterize mapping units, which will occur on numerous watersheds, thereby reducing the need to intensively sample all watersheds. Models driven by characteristics weighted by the area of each mapping unit in the watershed would be used to categorize the response of each watershed.

Results could be aggregated to test the initial regional categorization and to give numbers of lakes in each category for the population of lakes as a whole.

2.3.5 Data Needs and Availability

Referring back to the conceptual framework diagrammed in Figure A.2.1 (Section 2.3.1) as well as the discussion of controls on soil and water acidification in Section 2.2, we can list the data needed as input for a qualitative assessment or quantitative computer model (Table A.2.1).

Very few of these data are available in a digitized database useful for a regional direct/delayed/capacity protected assessment. Maps are available for regional inputs, but many of the controls on inputs listed vary on a local scale as discussed in Section 2.2.1. Limited data on soil characteristics (texture, drainage, organic matter, pH) are available in the SCS Soils-5 database. More chemical data are available in the SCS Pedon database, but the available soil series for northeastern forest soils are limited, chemical characteristics such as BS and CEC are based on a buffered pH, and verified, digitized files are not yet available. Further discussion on data availability and quality is found in Section 3 below.

2.4 SUMMARY

Figure A.2.7 shows the mechanisms hypothesized to be most important in controlling surface water acidification, along with watershed characteristics thought to determine whether each mechanism in fact is operational in a given watershed. Atmospheric strong-acid inputs drive the acidification process. For watersheds where most water reacts with the soils, cation exchange relationships, which control the salt effect and base cation buffering mechanisms, ultimately are the critical determinants of surface water acidification.

Table A.2.1. Data needs for direct/delayed/capacity-protected categorization of each numbered heading depends on the subheadings listed under it as well as on all headings above it.

---

1. Input Ion Concentrations, Loading
   - *location
   - *climate
   - *physiography
   - *canopy type
   - seasonality

2. Soil/Sediment Contact
   - hydrologic flow paths
   - flow rate, reaction time
   - soil texture, drainage, flow restrictive layer

3. Weathering Replacement
   - weathering rates
   - soil mineralogy
   - *bedrock type

4. Anion Retention
   - Sulfate
     - SO_4^{2-} retention capacity
     - percent capacity filled
     - solution concentration by evapotranspiration
     - biological accumulation

   - Nitrate
     - nitrogen status of ecosystem
     - nitrification rate

5. Base Cation Buffering
   - *base saturation
   - *cation exchange capacity
   - cation selectivity
   - aluminum solubility
   - vegetation withdrawal and redistribution

6. Salt Effect Alkalinity Depression
   - *base saturation
   - weak acid buffering
   - pCO_2 dynamics

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* Shows data available in at least limited form in a regional data base (see text for limitations).

Sulfate and nitrate retention largely determines the concentration of strong acid anions available in solution to balance protolytic and base cation leaching. Thus, sulfate and nitrate retention and base cation buffering are capacity factors that determine the delay that will occur before the salt-effect alkalinity depression/pH depression (intensity factor) takes place. Biological productivity generates alkalinity and help control nutrient ion distribution, thereby influencing the length of delay. Weathering replacement and atmospheric base cation inputs control the rate of base cation resupply to exchange sites, thus affecting the cation exchange relationships controlling cation leaching and the salt-effect alkalinity depression. Weathering rates may increase to keep up with strong acid anion deposition and leaching, or may at least reduce the rate of net loss of base cations from exchange sites. Hydrologic flow paths through a watershed determine if, where, and at what rate all of the soil/rock/sediment/biological reactions occur. Because soil characteristics vary with depth through the soil profile and regolith/till to bedrock, the predominant pathways and rates of flow of water through the watershed will determine which exchange, sorption, weathering, or biological reactions take place.

Each of these mechanisms is reasonably well understood conceptually and theoretically and has been incorporated into process oriented, predictive models. The models have been developed and calibrated based on existing data sets, but are just beginning to be tested/validated/improved using data.

Suitable laboratory or field data substantiating that each mechanism occurs, or their interactions in a whole watershed, are available for only a limited number of field sites or watersheds. Watershed data suitable for making a statistically valid, predictive regional assessment or classification of watersheds into direct, delayed, capacity-protected categories do not currently exist.

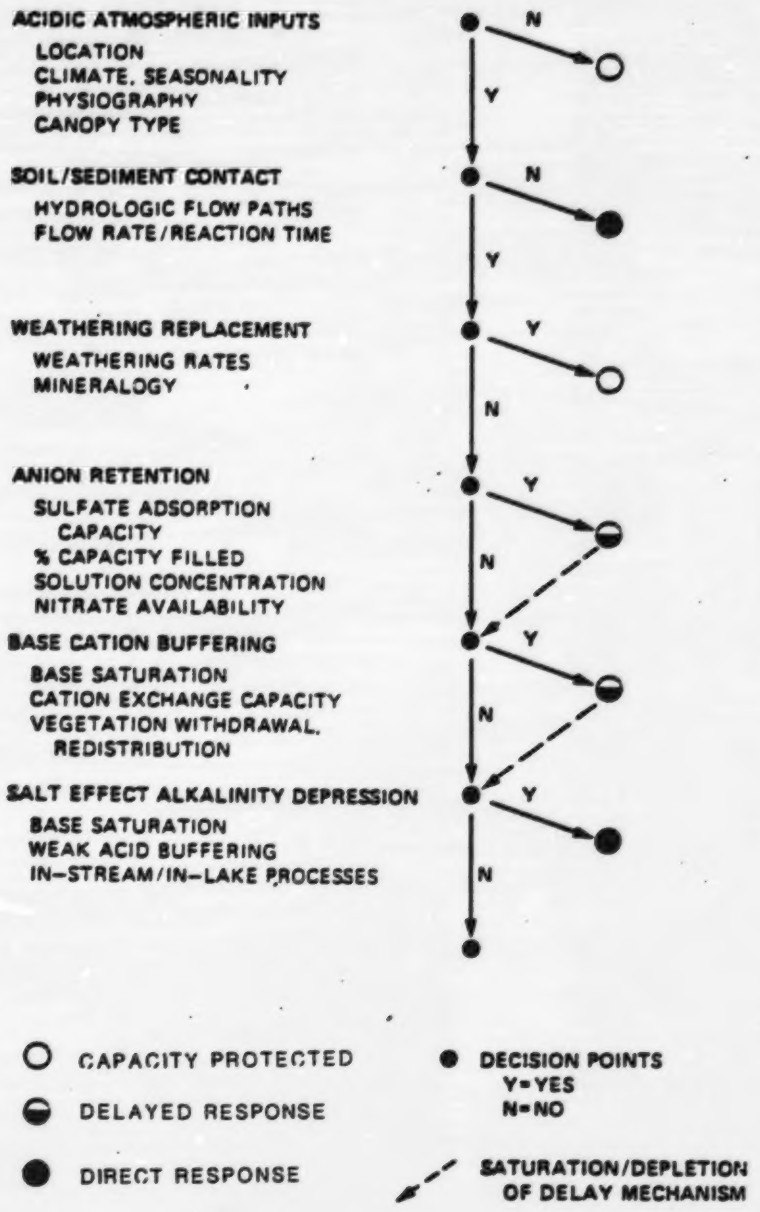

Figure A.2.7. Decision chart showing mechanisms hypothesized to be important in controlling surface water acidification. Arrows point to direct/delayed/capacity-protected outcomes (symbols), depending on which mechanisms are controlling in a given watershed. Subheadings indicate environmental factors thought to control each mechanism.

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Chapter 3

Current Understanding of Key Factors Hypothesized to Control Surface Water Acidification

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3.0 CURRENT UNDERSTANDING OF KEY FACTORS HYPOTHESIZED TO CONTROL SURFACE WATER ACIDIFICATION

3.1 INTRODUCTION

This chapter examines in more detail each of the processes or related groups of processes that we expect are key in controlling surface water acidification. These interacting processes are all integral to the conceptual framework outlined in Figure A.2.1 (Section 2.3), and form the basis for each decision point in Figure A.2.7 (Section 2.4). For each process we will examine its relevance to the direct/delayed/capacity protected assessment, the underlying chemical theory, relationships with other factors, how it is measured, the reliability of existing data, regional differences evident in the data, whether and how existing data can be used in classifying watersheds or areas into the different response categories, or what additional data should be collected.

Conspicuously absent from this chapter is the top line of Figure A.2.7, controls on atmospheric inputs. The direct/delayed/capacity protected assessment has been planned to date on the assumption that we know the regional patterns in deposition, and that they will continue at a more or less constant level. The predictive models can be manipulated to test for increases and decreases in deposition, should we desire to test "what if" scenarios. As was pointed out in Sections 2.2.1 and 2.2.2, however, we do not in fact know the inputs to individual watersheds or even with much confidence to subregions. For example, we can calibrate the predictive models on input-output data for one watershed, then move to a neighboring watershed that should have "similar" inputs, but which lies on a different aspect slope, and have no idea what the uncertainty is that we introduce into the evaluation. Clearly, this assessment must remain highly uncertain until we understand and can quantify better the between-watershed variation in inputs.

3.2 HYDROLOGIC PATHWAYS

3.2.1 Importance to Direct/Delayed/Capacity Protected Assessment

The flowpaths that water follows from the atmosphere to surface waters determine which biogeochemical reaction or exchange sites the water is exposed to. The rate of flow past those sites, and the seasonal differences in biogeochemical reactions, are critical in determining how the water chemistry will be altered as it passes through the watershed. The relative mix of water from different hydrologic pathways (e.g., rapid, shallow throughflow vs. deep groundwater baseflow), each with different chemical attributes, determines the chemistry of the surface waters, along with processes occurring within the sediments and water columns of the streams and lakes themselves. In general, acidic deposition that enters low alkalinity surface water by direct deposition, or by overland flow with minimal interaction with soils and vegetation, may acidify the surface water rapidly (direct response). On the other extreme, water which percolates through deep till or deeply weathered soils to appear in surface water as baseflow is likely to have adequate contact time with weatherable minerals to develop substantial alkalinity, and never contribute to surface water acidification capacity protected). Water that flows more rapidly as lateral flows through shallow soils may or may not contribute to surface water acidification, depending on the many chemical and biological processes occurring along those flowpaths (may be direct, delayed, or capacity protected).

3.2.2 Theory and Measurement

Water does not flow uniformly within a watershed. Canopy types (e.g., deciduous, coniferous) influence the amount of water that reaches the soil beneath them. Even snow is distributed nonuniformly across a watershed due to uneven topography and different vegetation types. Once water reaches the ground (or snow melts), it moves along preferred paths on the surface and through the soil. Water flows overland in rills and gullies and, if it infiltrates through the soil, it moves through macropores (large natural cracks or "pipes" in the soil, including channels created by tree roots) and meso-micropores (tiny pores in the soil that slow water movement and allow the acids in the water to react more with the soil). The movement of water also depends on the time of year; typically, it is more rapid and widespread during spring snowmelts or seasons when evapotranspiration is low. In certain watersheds, more water may reach the ground when deciduous trees have lost their leaves. How fast, when, and where water moves determines the extent to which biogeochemical processes alter the acidity of soil solutions and contribute to acidification or recovery of lakes and streams.

Recent advances in hydrologic research have established the important roles of variability in soil physical properties (Smith and Hibbert, 1979; Sharma and Luxmoore, 1979), of soil macropores (Thomas and Phillips, 1979; Beven and Germann, 1982), of convergent subsurface flow, and of variable contributing areas (Sklash and Farvolden, 1979) in determining runoff pathways during rainfall events. In addition, there are strong temporal effects on hydrologic processes determined by rainfall intensity at short time scales (<1 h) and by evapotranspiration at seasonal time scales. Depletion of stored soil water by vegetation during the growing season is accompanied by reduced streamflow. These spatial and temporal aspects of hydrologic processes may determine the areas within watersheds and timeframes of importance in assessing the response of the watersheds to acidic deposition.

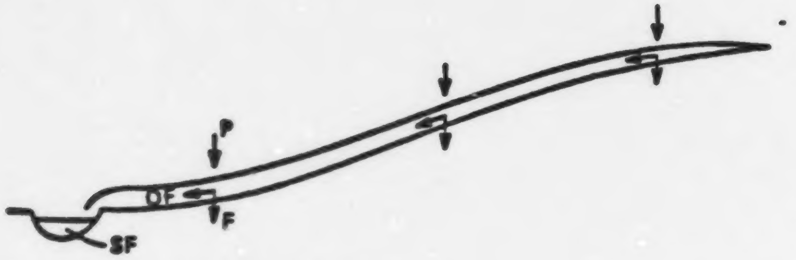
3.2.2.1 Background

Research over the past 20 years has shown that intermittent and perennial streams transport water derived from a variety of sources within a watershed. Because water in each flow pathway has a different residence time (time spent in contact with the terrestrial component) and comes in contact with different materials, its chemistry will vary from that of waters following other pathways. Consequently, the rate of discharge and the aquatic chemistry in a stream is a function of the flow rate, chemistry, and timing of individual flow components emanating from the terrestrial system. A stream is therefore an "integral response" of a watershed to water inputs. To understand the flow and chemistry in a stream, one must have knowledge of the individual flow pathways and biochemical reactions occurring along these pathways in the terrestrial system.

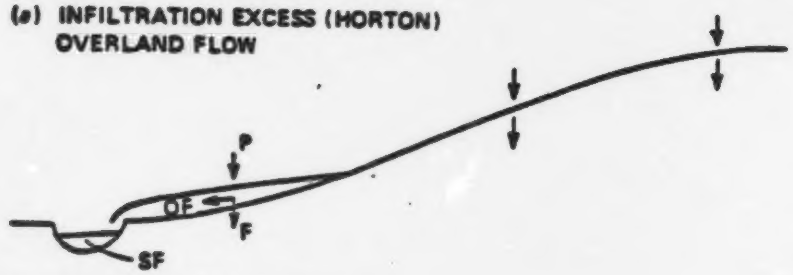
Considerable effort has been expended in attempting to understand the processes responsible for the generation of high flow episodes in streams during rainstorm and snowmelt events. Many theories have been advanced, and substantiated in some cases, regarding the complex and dynamic flow paths of water from the uplands and hillslopes of a watershed to the receiving stream. One entire book (Kirkby, 1978) has been devoted to the specialized topic of hillslope hydrology and covers conceptual models, monitoring techniques, results of intensive field research, and mathematical modeling. Other investigations have also been reported extensively in the literature. Few of these studies have attempted to investigate, in tandem, the flow and chemical transport of individual flow pathways, or to determine the spatial location where key water-soil and water-rock interactions are occurring. Several research projects have postulated that the depth of unconsolidated materials (i.e., soils, glacial deposits, aeolian deposits) and the ratio of subsurface to surface flow control the neutralization of acid precipitation and susceptibility of stream water to acidification. In general, it is thought that greater subsurface flow and longer residence times within the watershed result in less susceptibility of the stream to acidification (Beven, 1981; Goldstein et al., 1984). Although some advances have been made in our knowledge of the nature of terrestrial hydrologic pathways and chemical transport mechanisms, it is mostly qualitative knowledge. Two areas of hydrologic research require quantitative determination. We need to know (1) how the rates and chemistry of flow in each major flow path component varies spatially within a watershed and between watersheds and (2) how the flow rates and chemistries of hydrologic flow paths vary temporally in response to a range of water influx rates (rainstorm and snowmelt events) and acidity levels. In turn, the results of these determinations will assist us in answering the larger question of how the receiving stream behaves as an integral response to these multiple, dynamic inputs.

3.2.2.2 Mechanisms of Streamflow Generation

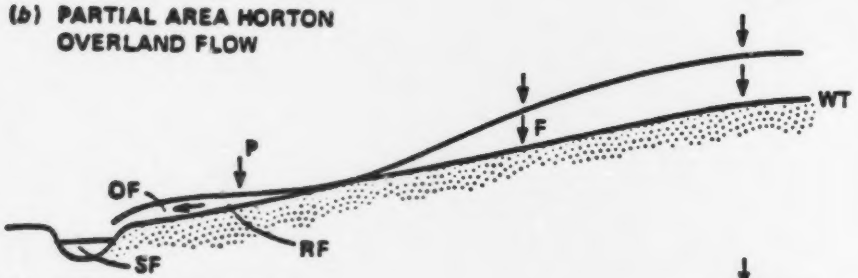
There are several theories as to how water moves from hillslopes to the receiving stream, and these are diagrammed in Figure A.3.1. Of these mechanisms, so-called infiltration excess, also known as Hortonian overland flow, is unlikely in a forested watershed. In contrast, partial area Hortonian overland flow, which occurs only in areas of low infiltrability, is a plausible process. According to this theory, overland flow is caused either by the local hydraulic properties of the soil (i.e., low permeability or insufficient pressure



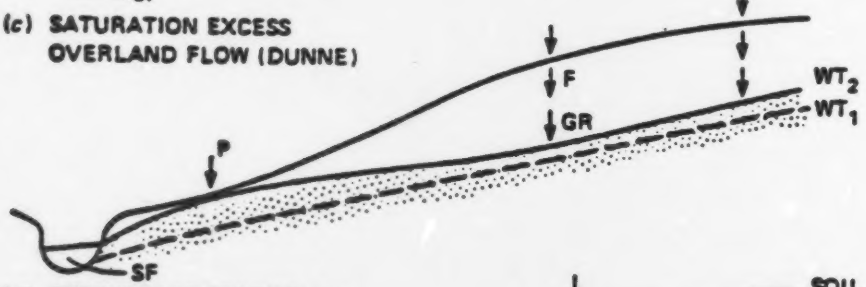
(a) INFILTRATION EXCESS (HORTON) OVERLAND FLOW



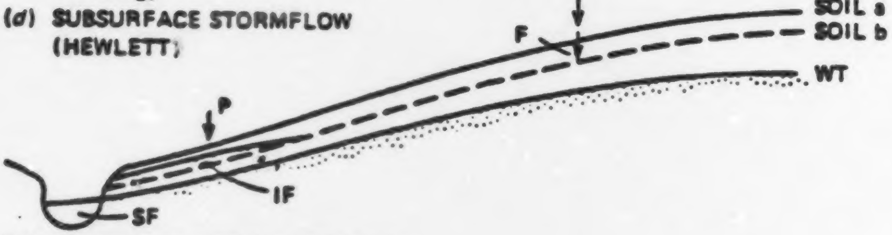
(b) PARTIAL AREA HORTON OVERLAND FLOW



(c) SATURATION EXCESS OVERLAND FLOW (DUNNE)



(d) SUBSURFACE STORMFLOW (HEWLETT)



(e) SATURATED WEDGE INTERFLOW (WEYMAN)

Figure A.3.1. Theories of water flow from hillslopes to receiving streams.

gradients) or by wet antecedent conditions (or by both). The area of the watershed that contributes overland flow to the stream is termed the "variable hydrologic source area." Understanding the dynamics of these source areas is central to understanding the watershed response to a storm. In the partial area concept, the variation in the source areas within a storm is attributed mainly to the temporal variation of storm intensity, whereas the variation in source areas between storms is largely due to antecedent moisture conditions. Where the partial area concept is applicable, streamflow would be expected to be a mixture of groundwater (baseflow) and overland flow. In this conceptualization, lateral subsurface flow in the unsaturated zone is considered to be negligible. With the de-emphasis on lateral subsurface flow, it follows that water sampling under this regime could be limited to surface and groundwater collection near the stream itself. The partial area concept with no provision for subsurface routing has been used successfully to simulate storm-event hydrographs for large storms over watersheds of mixed land use by V. Shanholtz and others at Virginia Polytechnic Institute (see articles by Ross et al., 1979; 1980). In contrast, other conceptual models of streamflow generation assign a significant role to lateral subsurface flow. In the case of saturation excess, surface runoff is a mixture of overland flow and shallow subsurface water. The increase in the subsurface flow component during a storm is directly related to the dynamic expansion of the source area. Thus, the runoff mechanism can yield "flashy" stream discharges; that is, once the system saturates the nearstream areas, additional rainfall expands the source area.

In the subsurface stormflow mechanism, the rapid response of the rising water table is sufficient to generate increased seepage, which accounts for the increased streamflow. In this case, streamflow is expected to be predominantly "old" water that has been in contact with the soil phase for an extended period. If transport in the porous medium is via macropores, however the resulting chemistry may be more complicated.

The saturated-wedge-interflow mechanism is similar to the previous subsurface mechanism except that the mobile soil water collects in a transient, perched water table above a less permeable soil stratum. If the water table rises and intersects the surface, a source area is generated and an overland pathway occurs. Water chemistry is expected to reflect the watersoil interactions specific to all the saturated soil layers. In reality, runoff production within any natural watershed is probably a complex combination of all of these mechanisms. As the soil gets wetter, the system can change from predominantly subsurface flow to saturation overland flow. Moreover, during a storm, different mechanisms operate in different parts of the watershed. The three issues that are most relevant to understanding the behavior of watershed response are soil heterogeneity, macropore flow, and dynamic response of hydrologic source areas.

3.2.2.3 Soil Heterogeneity

The hydrologic role of vertical heterogeneity (i.e., soil layering or soil horizons) is fairly well known, although it can be hard to reconcile with the traditional tendency to view the soil system as an array of isolated vertical soil columns. However, the consequences of lateral variability in the hydraulic properties of soil are poorly understood. Stated in qualitative terms, within a natural soil system, some parts will be more sandlike (more permeable) than the overall average soil, whereas other parts will be more claylike. Mathematically, these varying hydraulic conditions are encapsulated in the so-called "scaling factor," which relates the unsaturated moisture characteristic and the hydraulic conductivity function of a specific point to the same functions of the "average soil" (Clapp _et al._, 1983). In general, the scaling factor itself is viewed as a random variable with a frequency distribution specific to a given soil system. In this way it has been used to simulate the effects of randomly distributed soil properties on watershed water budgets (Peck _et al._, 1977; Sharma and Luxmoore, 1979; Luxmoore and Sharma, 1980) and on the variability of soil moisture itself (Clapp _et al._, 1983). One key difficulty with past studies is that they have viewed the distribution of soil heterogeneity, as represented by the scaling factor distribution, as totally random, whereas experience suggests otherwise. Such a pattern would enhance the development of variable source areas, thereby affecting runoff production. A key challenge in physically based watershed modeling is identifying the random and nonrandom spatial variability in the hydrologic behavior of soil and quantifying it.

3.2.2.4 Role of Macropores

It is generally acknowledged that in forested watersheds significant portions of subsurface flow occurs in soil macropores, although quantitative estimates are difficult to make. Beven and Germann (1982) provide a comprehensive review of the hydrologic research related to macropores. There are two main viewpoints as to the possible relationship between macropores and the capillary pores in the soil fabric, and the differing viewpoints have important implications for how the soil system operates, for the experimental methods used to identify the system components, and for the synthesis of the experimental results.

In the extreme, large channels caused by roots and animals plus soil cracks and fissures can conduct water through the system when the surrounding soil matrix remains largely unsaturated. This condition suggests a two-continuum model in which large pores and the capillary pores act as different, but interconnected, transport systems. Quantitative models of this type are just beginning to be formulated, AGTEHM (Hetrick et al., 1982) being one example, but it is safe to say that there is no generally accepted mathematical representation of the two-continuum system.

In a simpler conceptualization, large pores are considered to yield an abrupt increase in hydraulic conductivity as the soil moisture approaches total saturation. With this conceptualization, regular diffusive models can be applied, although there remains a key problem in identification of a representative control volume for assessing the basic hydraulic properties of the soil. The volume must be large enough to contain an average number and size of macropores yet retain an internal homogeneity of physical and chemical properties.

The presence of macropore flow has important implications for almost every aspect of experimental field work. Tensiometers and suction lysimeters traditionally used to measure water pressure and to sample soil water, respectively, in the unsaturated zone provide less meaningful data in soils containing hydrologically active macropores. This is so largely because of the uncertainty of sampling a randomly occurring large pore and, to a lesser extent, because these samplers with their porous ceramic sampling surfaces are slow to react relative to the fast flows expected in the large pores. Where macropores occur, it is best to sample flows by digging trenches and installing subsurface weirs or by putting collection pipes directly into a flowing pore.

3.2.2.5 Variable Source Areas

Although the concept of source areas for the generation of overland flow has attained wide acceptance, researchers have seldom mapped overland flow either directly by observation or indirectly by calculation and modeling [significant exceptions include the studies by Rogowski _et al._ (1974) and Beven _et al._ (1984)]. The most reliable method for direct measurement is to simply walk around the low, wet areas of the watershed during a storm and look for saturated conditions underfoot. Beven has used an array of simple T-shaped collectors with the lower tube buried in the soil. The presence of water in the collector array provides a map of the largest extent of the source area for the particular rainfall event.

A more elegant and quantitative method is based on the assumption that source areas remain wetter than other parts of the watershed during interstorm periods. With an array of tensiometers, the dynamic behavior of these areas can be monitored while moisture continues to move downslope under unsaturated conditions (with or without macropores contributing to that flow). This approach was pioneered by Anderson and Burt (1978) and Anderson and Kneale (1982). From a practical viewpoint, the present limit to the number of tensiometers that can be monitored simultaneously is about 25 to 50, and given the heterogenities one might expect, this limitation implies that only a small subarea of a watershed can be monitored effectively.

3.2.2.6 Measurement of Flow Components

Several methods are available for dividing streamflow into individual flow components (Table A.3.1). The oldest technique, which is still often used with several variations, is to measure actual streamflow and to interpolate the groundwater baseflow from one nonstorm period to the next. Flow below the "baseflow curve" is groundwater discharge; all remaining flow of storm hydrographs is derived from macropore flow and overland runoff (event water). Several publications discuss the various methods and uses of classical hydro-

Table A.3.1. Methods of discriminating terrestrial flow components in streamflow.

---

1. Calculation methods
    - A. Stream hydrograph separation
    - B. Hydrometric monitoring and mathematical simulation
    - C. Groundwater well calibration

2. Direct physical measurements
    - A. Runoff from hillslopes
    - B. Seepage trenches
    - C. Seepage meters
    - D. Streamflow monitoring
    - E. Tracer dilution

3. Chemical budgeting
    - A. Cations, anions, specific conductance
    - B. Natural isotopes (T, D, ^{14}C, ^{18}O, ^{34}S, ^{222}Rn, N)
    - C. Dissolved organic carbon

graph separation techniques (Huff and Begovich, 1976; Pettyjohn and Henning, 1979).

Knowledge of hydraulic head distribution, hydraulic conductivity, and other hydraulic characteristics of soils, unconsolidated materials, and bedrock in the vicinity of a stream (or lake) can be used to calculate the steady-state or transient discharge rates of groundwater (saturated soil and bedrock flux). The calculation methods can range from simple analytical equations to complex numerical techniques. Stratigraphic information, hydraulic head distribution, and pumping test results obtained from nested piezometers along the streams would be necessary for saturated groundwater flow calculations.

A third method (method 1-C, Table A.3.1) of calculating the groundwater flow component of a stream can be done by groundwater well calibration. An empirical relationship between groundwater levels in piezometers and ground water discharge in a nearby stream is developed for various levels of baseflow during nonstorm periods. This groundwater stage vs groundwater discharge rating curve technique has been applied by Rasmussen and Andreasen (1959), Schicht and Walton (1961), and Sklash and Farvolden (1980). Sklash and Farvolden (1980) applied this method to an agricultural watershed in Ontario and found approximately 80% of runoff from one storm (10 cm of rainfall over a four-day period) was groundwater from a thick sand unit.

Direct physical measurements of flow into a stream can be made at surface discharge locations along the sides of a stream channel. Flow of surface runoff in discrete gullies, distinct springflows (at slightly higher elevation than the stream), and diffuse seepage areas can be physically measured by a variety of methods (e.g., weirs, flumes). Seepage rates through various soil layers and subsurface materials can be measured in trenches dug upslope and parallel to the stream. These seepage-monitoring trenches can be constructed and instrumented in a variety of ways, as discussed by Atkinson (1978). The disadvantages of this technique are the difficulties often encountered in continuous monitoring of flow and the short length of stream bank that is actually monitored.

Seepage and distinct springs in a streambed beneath the water level are much more difficult to detect, monitor, and sample. Seepage meters (Lee et al., 1978; 1980) could be used, but the successful use of such meters may be improbable. They sample only a small surface area, and placing them in a cobble or gravel streambed would be impossible. However, their use is recommended for measuring and sampling groundwater flux through the lakebeds.

Other direct measurements in the stream can be used to determine groundwater contributions to individual stream reaches: (1) The entire stream can be diverted through a flume or pipe, and the seepage rate into the riverbed can be directly measured; this would probably be possible only during baseflow periods or small storms. (2) Streamflow can be measured at two different points, and if no surface tributaries exist between the measuring points, the difference in flow is due to groundwater discharge in that reach of the stream. (3) Dye or another tracer can be added at a steady rate to the stream (during constant-flow periods) and allowed to mix thoroughly; then the amount of dilution found in a downstream direction is due to groundwater inputs.

The third approach to streamflow deconvolution is by chemical budgeting. If the chemical composition of each terrestrial flow component (e.g., surface runoff, macropore flow, slower soil water seepage, groundwater baseflow) is known and each component has a distinguishing characteristic different from the other components, then it is possible to separate the flow contribution of each component in the streamflow. If two sources of flow enter a stream, then

$$Q_sC_s = Q_1C_1 + Q_2C_2 \qquad (1)$$

$$Q_1 = Q_s(C_s - C_2)/(C_1 - C_1) \qquad (2)$$

$$Q_s = Q_s(C_s - C_1)/(C_2 - C_1) \qquad (3)$$

Thus, if the time-dependent flow rate of the stream (Q_s) and concentration of the chemical variable (C_s) are known for the stream and for two contributors to streamflow, then the flow rates of each flow component (Q_1, Q_2) can be determined. If the chemical variables (C_1, C_2) are distinctly different for each of two flow components, then a much more reliable estimate of flow rates can be made. If three types of terrestrial flow paths contribute to a stream, then more chemical variables and equations would be needed to calculate the three unknown flow rates (Q_1, Q_2, and Q_3).

Regular chemical variables, such as calcium, magnesium, sodium, manganese, chloride, sulfate, fluoride, and specific conductance can be used if their concentrations are distinctly different in each terrestrial flow component. Several previous studies have used chemical mass budgeting to separate streamflow into two components -- baseflow and event water (Newberry et al., 1969; Pinder and Jones, 1969; Pilgrim et al., 1979). Normally, the concentrations of variables in event water and baseflow water are considered constant with time to complete Eqs. (1) and (2). However, two complications may arise. There is some evidence that an initial flush of solutes is carried with overland flow and shallow macropore flow during the early part of storms. The second complication arises because there should be an increase in solute concentration in each flow component in poststormflow as the time of contact between water and geologic materials increases. These complications can be overcome if the time-dependent change in chemical concentrations of all flow components are known during each storm event (Pilgrim et al., 1979).

Environmental isotopes (e.g., T, D, ^{18}O) have commonly been used in the past for separating baseflow from runoff and shallow macropore flow contributions to streams. The advantages of using isotopes are (1) the isotopic composition of event water is often very different from groundwater baseflow, (2) isotopic concentrations of terrestrial flow path components are not as susceptible to transient solute flushes and concentration variations during individual storm events, and (3) in some cases, the isotopes (particularly tritium) can provide some information on the absolute age and relative residence time of water in the subsurface. Examples of studies in which these isotopes have been used for hydrographic separation purposes are presented by Mook et al. (1974) and Sklash and Farvolden (1979, 1980, 1982).

The measurement of D, T, and ^{18}O as a means of discerning flow paths for major snowmelt water may be greatly advantageous over chemical variables. Most ionic constituents are generally flushed from snowpacks in the early periods of snowmelt, and concentrations rapidly decrease. However, the isotopes tend to be homogenized in a snowpack during the winter, and their concentrations in snowmelt are relatively constant through time (July et al., 1970, Dancer, 1970), thus reducing the problems of following snowmelt through the hydrologic system. Dancer et al. (1970) showed that snowmelt in a watershed partially above the tree line contributed about 33% of the peak streamflow in spring; the remainder of snowmelt infiltrated to the groundwater reservoir and displaced groundwater of snowmelt origin from previous years.

Although not widely reported in the literature, other isotopes such as ^{34}S, ^{14}C, ^{13}C, and ^{15}N can be used to identify and perhaps date the subsurface flow components contributing to streamflows. Krothe (1982) presents some examples of how ^{34}S can be used to differentiate groundwaters of different sources. Some very preliminary analyses of ^{222}Rn for one watershed in Ontario have shown that groundwater is enriched in ^{222}Rn (as would be expected) and is significantly different from event water (Sklash and Farvolden 1982). A field-portable radon detector was used in this research, so if this isotope could be investigated further, it could greatly reduce the cost of other time-consuming isotope analyses.

One other available chemical that may be a useful indicator of different flow pathways is dissolved organic carbon (DOC). However, investigative and developmental work would first be required.

3.2.3 Adequacy of Existing Data for Regional Assessment

Given the difficulty of directly measuring hydrologic pathways through different types of watersheds, it is no surprise that very little data exists for individual watersheds or for assessing regional patterns.

3.2.3.1 ILWAS Case Study

The Integrated Lake Watershed Acidification Study (ILWAS) was specifically designed to study the causes of Adirondack lake acidification, and provides some of the clearest evidence of the importance of hydrologic pathways in controlling surface water acidification in that region. Results of an intensive study of watershed hydrologic characteristics of two watersheds are reported in Murdoch et al. (1984), and summarized in Goldstein and Gherini (1984). The importance of hydrologic pathways in controlling acidification, and some of the measurements and analyses needed to reach that conclusion, can be seen from the summary paragraphs of the project-summary volume, quoted below (from Goldstein and Gherini, 1984).

"The relative amount of precipitation which follows shallow versus deep flow paths within a watershed is thought to influence the response of a lake to acidic precipitation. In watersheds with deep permeable soils and hence large ground water storage capacities, more of the precipitation will percolate into the deeper horizons and remain there for longer periods allowing for further alkalinity-producing reaction with the surficial geologic materials.

"Analysis of the hydrographs show that runoff from Woods Lake responded quickly to precipitation events and had a very small baseflow. The runoff from Panther Lake is less dynamic and had a larger baseflow component. Estimates of change in ground water storage over winter and summer periods, on a water-equivalent depth basis, are 6†cm for Panther and 2 cm for Woods, based on ground water level data, and 6.9 cm and 1.8 cm, respectively, based on an analysis of recession rates. Monthly water budget calculations also show higher ground water recharge in fall and spring and greater drawdown in the winter in Panther Lake basin than in Woods Lake basin. All the above analyses indicates a larger, more active ground water reservoir in the Panther system.

"The lateral flow capacity of the mineral soil horizons was estimated for both basins to determine if this capacity can be exceeded by the rate at which water is applied to the soil. The maximum flow capacities in terms of applied precipitation were 20 cm/yr for Woods and 650 cm/yr for Panther basin. The actual net precipitation (that not lost to evapotranspiration) was about 75 cm/yr in the basins. Thus, most of the applied water in Woods cannot pass through the mineral soil horizon primarily due to its smaller cross-sectional area; the flow instead "backs up" into the shallow acidic organic soil horizons. At first, it would appear that the lateral flow capacity would not be exceeded in Panther basin. However, during the snowmelt period, up to three months of accumulated precipitation may melt in about two weeks. This melting applies water to the soil at a rate equivalent to about 900 cm of precipitation per year. During snowmelt, the lateral flow capacity of the mineral horizon was most likely exceeded in Panther basin. The bypassed water would be expected to be acidic. Surface water quality data during snowmelt show large pH and alkalinity depressions in Panther Lake" (Goldstein and Gherini, 1984).

Preliminary results from over 20 additional Adirondack lake watersheds in the Regional Integrated Lake Watershed Acidification Study (RILWAS) reinforce the importance of depth of surficial materials (till), though there are some other factors also (S. A. Gherini, personal communication).

3.2.3.2 Regional Extrapolation

Examination of RILWAS data on hydrologic pathways for relationships which may aid in assessing hydrologic characteristics on a regional scale is needed. For example, is the depth of till an adequate measurement to characterize hydrologic flow paths, or would additional data on soil texture, presence of a restrictive layer, or other characteristic help out? Are there other data in available data bases that correlate well with the measured characteristics and that could be used as surrogates for actual measurements? Can stream density, or other physiographic factors that can be easily analyzed by a computerized geographic information system (GIS), be related to hydrologic characteristics? Can published USGS storm-hydrograph data or flooding frequency data show regional differences in hydrologic characteristics that are useful to the direct/delayed response assessment? It must also be established how these relationships hold up in regions other than the Adirondacks. For example, is the depth-of-till generalization useful in Maine, or are other factors more important there?

We know generally that hydrologic characteristics of nonglaciated regions are quite different from glaciated areas, but there are many unknowns. Is macropore flow more important in clayey southeastern soils than in relatively coarse-textured northeastern soils? How do climatic differences between the two regions affect flow paths? We can qualitatively assess differences between the two regions, but there has not been an ILWAS-equivalent study performed in the southeast. There is one RILWAS site at Coweeta, North Carolina, a subsurface transport study underway at Oak Ridge, Tennessee, and macropore studies ongoing at Clemson, South Carolina. However, these are small-scale, individual studies that can not lead to the integrated understanding of watershed hydrologic behavior that was reached for the ILWAS sites.

In summary, we may be able to extend the depth-of-till generalization to characterize hydrologic behavior for the Adirondack region, and possibly other mountainous, glaciated areas of New England, though this should be tested. More research is needed to determine hydrologic relationships in low-elevation or lower-relief glaciated regions and in unglaciated regions.

3.3 ANION MOBILITY

3.3.1 Importance to Direct/Delayed/Capacity Protected Assessment

Atmospheric acid deposition will have no affect on the acidification of surface waters if the anions associated with the acid, SO_4^{2-} and/or NO_3^- , are not mobile in the soil. In some cases, an ecosystem may retain incoming SO_4^{2-} or NO_3^- for a period of time until a "breakthrough" occurs, thus resulting in a delayed-response system.

3.3.2 Chemical Theory

The concept of anion mobility is gaining recognition as a useful tool for both understanding and assessing the effects of acid precipitation on elemental leaching. This concept, first introduced by Nye and Greenland (1960), revolves around the fact that total anions must balance total cations in solution.

Since soils typically have more cation than anion exchange or adsorption capacity and since anion concentrations are controlled by more or less independent mechanisms, it is useful to visualize total ionic leaching as a result of the introduction of mobile anions to soil solution (Johnson and Cole, 1980).

With respect to acid precipitation, it has been repeatedly demonstrated that sulfate adsorptionoccurs insome soils, and can prevent the leaching of either nutrient cations or H^+ and Al^{3+} (Johnson and Cole, 1977; Singh et al., 1980; Lee and Weber, 1982) whereas the reverse is true when sulfate is not adsorbed (Cronan et al., 1978; Mollitor and Raynal, 1983).

Nitrate is increasingly associated with acid precipitation and differs considerably from sulfate in that it is very poorly adsorbed to most soils (Johnson and Cole, 1980). Nitrate, however, is quickly immobilized by biological processes in N-limited ecosystems, and since N-limitations are common in forested regions of the world, nitrate is rarely mobile (Abrahamsen, 1980). The are notable exceptions, however, in sites that are naturally N-rich (e.g., by the presence of N-fixing species; Van Miegroet and Cole, 1984) or are subjected to excessive atmospheric N input (Van Breeman et al., 1983). In those cases, N inputs in any form in excess of biological N requirements have resulted in nitrate mobility and/or internal production of additional nitric acid through the process of nitrification.

3.3.3 Sources and Sinks

Forest vegetation has little capacity to biologically accumulate the cycle-excess S. The net annual accumulation of S in forest biomass (i.e., in woody tissues) accounts for only a fraction (approximately 10%) of that which cycles in forest ecosystems, as is the case for most nutrients in forest ecosystems.

Thus, forest requirement for S from sources external to the biological S cycle (i.e., from the mineral soil or the atmosphere) are quite modest. Humphreys et al. (1975) suggested that atmospheric S inputs as low as 1 kg/ha-yr may be sufficient to supply forest S needs in Australian Pinus radiata stands.

Despite relatively low biological S requirements, several forest ecosystems in the southeastern United States appear to be accumulating S (Smith and Alexander, 1983). As noted by Haines (1983), the "apparent" net SO_4^{2-} accumulation in these ecosystems could in theory be due to a number of factors, including tree uptake, incorporation into soil organic matter, soil SO_4^{2-} adsorption, precipitation of Al-SO_4 minerals, organic S leaching, and reduction and volatilization of H_2S, dimethyl sulfide, or other gaseous S compounds. The latter two processes constitute unmeasured losses and might lead to a balanced S budget.

Tree uptake is unlikely to be of sufficient magnitude to account for differences in SO_4^{2-} inputs and outputs, but incorporation of SO_4^{2-} into soil organic matter may constitute a large net SO_4^{2-} sink (Swank et al., 1984). Measurements of S losses by volatilization and organic S leaching are rare, but available measurements suggest that whereas these fluxes are not necessarily insignificant, they would generally be too low to account for SO_4^{2-} input-output imbalances (Haines, 1983: Adams, 1980).

Several factors suggest that SO_4^{2-} adsorption (and, in some cases, perhaps co-precipitation with Al) account for a large portion of apparent net SO_4^{2-} accumulation (where it occurs) in forest ecosystems. First, there are correlations between SO_4^{2-} adsorption properties of soil and apparent SO_4^{2-} accumulation in the system (Johnson and Todd, 1983). Second, where lysimeter budgets are available for estimating fluxes through various soil horizons, net SO_4^{2-} accumulation (i.e., input > output) usually occurs primarily in Fe- and

Al-oxide rich subsurface horizons (except in Spodosols, where organic matter blocks adsorption) rather than in organic matter-rich surface horizons. Finally, artificial additions of SO_4^{2-} often result in net SO_4^{2-} retention in soils, even when SO_4^{2-} budgets with ambient inputs were in steady-state (Johnson and Cole, 1977; Lee and Weber, 1982; Singh et al., 1980), a finding consistent with the concentration-dependent nature of soil SO_4^{2-} adsorption and precipitation reactions.

Many forests are N deficient, and atmospherically-derived N is usually rapidly immobilized by ecosystem biota. This retention precludes NO_3^- losses (and associated cation leaching) and may even result in increased forest growth. However, exceptions occur when N supplies are excessively enriched, whether by natural processes (for example, N fixation), fertilization, or atmospheric inputs. Deposition of N in excess of forest requirements almost invariably leads to nitrification and nitrate leaching. Since oxidation of NH_4^+ results in direct input of H^+ to the soil (rather than to canopy and litter layers as is the case with acidic deposition) and in cation leaching, its effects on soil acidification can be pronounced.

3.3.4 Factors Affecting Anion Mobility

Each of the major anions in soil solutions -- bicarbonate, nitrate, chloride, sulfate, phosphate, and organic anions -- has some unique features with regard to the chemical and biological reactions into which it enters. The production and mobility of nitrate, for example, are regulated almost entirely by biological processes as discussed previously. The mobility (though not necessarily the production) of phosphate is most strongly influenced by adsorption and precipitation reactions. Sulfate and bicarbonate are intermediate, being affected by both biological and inorganic chemical reactions, whereas chloride is relatively unaffected by either type of reaction and is generally mobile in soils.

The anions of interest here, SO_4^{2-} and NO_3^-, are controlled by entirely different factors. Sulfate is often immobilized by adsorption and precipitation reactions, especially in sesquioxide-rich soils (Johnson and Todd, 1983) or by incorporation into soil organic matter (Swank et al., 1984).

Soil SO_4^{2-} adsorption is positively correlated with Fe and Al oxide content but negatively correlated with organic matter content (Johnson and Todd, 1983). Subsurface soils and organic-rich subsoils of Spodosols (podzols) are therefore inefficient SO_4^{2-} adsorbers, even if enriched in Fe and Al hydrous oxides. Subsurface horizons of Ultlsols, Oxisols, and certain suborders of Inceptisols and Entisols (Andepts, Psamments) are efficient SO_4^{2-} adsorbers and often result in net ecosystem SO_4^{2-} retention. However, the potential for retention of atmospherically deposited SO_4^{2-} in subsoils may be reduced to the extent that water flows through soil macropores or laterally through surface soils, bypassing these potential adsorption sites.

In comparison to SO_4^{2-}, NO_3^- adsorbs very poorly to most soils (exceptions occurring in soils extremely rich in Fe and Al oxides; Kinjo and Pratt, 1967). Factors affecting nitrification in forest soils are very complex, but significant progress in determining them has been made in recent years. Rice and Pancholy (1972) proposed that nitrification in late successional forests in Oklahoma was controlled by the production of nitrification inhibitors. On the other hand, Coats et al. (1976) and Johnson et al. (1979) found no evidence for the presence of inhibitors in litter extracts from coniferous forests in California and a deciduous forest in Tennessee, respectively. In both cases, the availability of ammonium substrate appeared to be the major limitation to nitrification, and this, in turn, was presumed to be regulated by the competition for N by heterotrophic soil organisms.

Vitousek and Reiners (1975) proposed that nitrate leaching in undisturbed forest ecosystems in New Hampshire was controlled largely by plant uptake. They supported this hypothesis by showing that streamwater nitrate concentrations were lower in watersheds with young, vigorously growing vegetation than in watersheds with mature ecosystems. In a later inter-regional comparison involving trenched plot studies in many parts of the U.S., Vitousek *et al*. (1979) found that nitrate production and mobility were controlled by four major processes: vegetative uptake, nitrogen mineralization, lag times in nitrification, and a lack of water for nitrate transport. They found that uptake by vegetation was insufficient to offset increases in mineralization and nitrification on fertile sites, and they concluded that such sites have the potential for very high nitrate losses following disturbance.

3.3.5 Effects of Acidic Deposition

As noted above, acidic deposition can contribute substantial amounts of sulfur and/or nitrogen to ecosystems. To the extent that either S or N is mobile in the soil solution, deposition above natural levels will result in accelerated leaching of cations from the soil and potentially could result in acidification. It is important to consider redox processes for both N and S (oxidation of SO_2 and NH_4^+) in the system, thus consideration must be given to total deposition (e.g., of SO_2 and NH_4^+) vis-a-vis biotic and abiotic retention capacities within the ecosystem.

3.3.6 Measurement of Anion Mobility

Mobility of nitrogen and sulfur has been widely described on the basis of field data; there has also been considerable effort to understand and describe sulfate mobility in laboratory studies. In the field, calibrated watersheds allow quantification of inputs and outputs from an ecosystem. There are certain drawbacks to this procedure, however; it requires a long-term and continuous monitoring program to get reliable measurements, and certain fluxes must be measured or estimated indirectly (e.g. dry deposition of SO_2, NH_4^+) or guessed at (e.g., sulfate reduction rates, internal S sources). A second problem is that the flux data cannot provide unequivocal answers about control mechanisms or capacities. Flux data are thus potentially subject to misinterpretation concerning processes and rates, and are of limited predictive value. Input-output budgets are extremely useful, however, in characterizing the net behavior of S and N; i.e., in quantifying the magnitude of net storage or releaes from a system. Budget data are also useful for making inferences about processes controlling S or N mobility, and are useful for comparing relative mobility of anions at different sites (e.g., north-south, forest stand type, or age comparison).

In the case of sulfate, soil pools are frequently quantified by laboratory procedures as "soluble" (i.e., adsorbed, but leachable with deionized water) or "adsorbed" (removable only by an anion such as phosphate which forms stronger bonds with the adsorbent than sulfate (Johnson and Henderson, 1979). The soluble pool is weakly bound, and is readily available for biological uptake or leaching from the soil. By contrast, "adsorbed" sulfate is much more tightly held on the soil, it is probably "specifically adsorbed" by ligand exchange (formation of one or two M-O-S bonds) or perhaps by formation of aluminum sulfate minerals (Nordstrom, 1982). Soluble sulfate is predominant in organic soil horizons or in soils with low sesquioxide content and low organic matter. The adsorbed sulfate pool may be irreversibly bound in soils, and is apparently the primary sink for inorganic sulfate in soils (Johnson and Henderson, 1979; Johnson et al., 1981). Existing sulfate pools in soil can be related to historical sulfate deposition (e.g., soluble plus "adsorbed" pool compared to cumulative historic deposition), but are of little direct use in predicting present or future input-output relationships.

To describe the capacity of soils to adsorb additional sulfate, a number of investigators have used adsorption isotherms (e.g., Chao et al., 1964; Singh, 1984); isotherms have been used both as tools to understand sorption behavior as a function of pH, soil Fe and Al content, etc. (e.g., Chao et al., 1964) and as a predictor of sulfate partitioning under field conditions (Cosby et al., 1984). In the latter case, the authors lumped data from several soil sites and depths, and developed an average isotherm for a watershed (X-axis as output flux of SO_4^{2-} eq/ha-yr; Y-axis as adsorbed pool in eq/ha). Using that isotherm in a dynamic model with various scenarios of annual sulfate deposition, the authors were able to use the model to recreate historic changes in dissolved sulfate in their study watershed, and to predict future changes.

3.3.7 Reliability of Measurements

The reliability of laboratory isotherm data for predicting sulfate dynamics in field situations is still uncertain, owing to uncertainty in flow path, biological cycling of sulfate, temperature effects, etc. Sulfate adsorption isotherms have been determined for only a few soil sin the eastern U.S., and analyses have been done at a limited number of laboratories; sample handling, equilibration conditions, and analytical protocols have not been standardized. Interpretation of data and applicability to field conditions is a subject to continuing debate. Sample handling, such as air drying the soil, and storage conditions, between the time of soil collection and analyses may have a significant impact on adsorbed sulfate pools and/or adsorption isotherms; the actual impact is at present unknown.

Given the dominant influence of biological processes, laboratory studies of nitrate mobility are useful in providing insight into the processes controlling mobility, but are unlikely to generate useful data concerning actual nitrate flux from the soil.

Field measurements are the most reliable indicator of sulfate and/or nitrate mobility for a specific soil/watershed system, but it is necessary to characterize seasonal- or discharge-related variability in mobility. In the case of sulfate, laboratory data on adsorption isotherms holds significant promise as a predictive tool, but at present such techniques must be used with caution.

3.3.8 Expected Range and Regional Distribution

Based on sulfate budgets for calibrated watersheds, sulfate retention appears to be much more significant in ecosystems of the southeastern U.S. than in the northeast (e.g., Likens *et al.*, 1977; Galloway *et al.*, 1980; Swank and Douglas, 1977; Henderson *et al.*, 1977). As previously noted, accumulation of sulfate by tree uptake can be discounted as a major immobilization mechanism. Incorporation of sulfur into soil organic matter may be important (David *et al.*, 1982; Swank *et al.*, 1984), but data are too sparse to allow any estimates of regional differences or significance for this process. Sulfate adsorption has generally been assumed to be the primary retention mechanism in southern soils (Ultisols and Dystrochrepts) while adsorption by northern Spodosols is believed to be low. This assumption is supported by data from the literature (e.g., Johnson and Todd, 1983), and also by data from EPA's pilot soil survey. The later study found total extractable sulfate (soluble plus adsorbed) to be 1.5 to 10 times as high in six Virginia soils as in soils from New York (Adirondacks) and Maine; the differences were most pronounced in the surface A-E horizons and in the C horizon.

Regionalization of potential NO_3^- mobility is far more difficult because biological processes are involved, but some qualitative insight may be gained by comparing N deposition rates to a very broad estimate of forest N requirement based upon nutrient cycling data (e.g., Cole and Rapp, 1981). Northeastern forests are most susceptible to NO_3 leaching according to this criterion, since forests are slower growing and presumably less demanding of N. A significant caveat to this approach, however, is that N uptake by soil biota, which is often a dominant form of N immobilization, is not accounted for.

3.3.9 Threshold Values

Mathematical models have been developed, based on adsorption isotherms, to describe time trends in sulfate mobility (e.g., Cosby et al., 1984). Such models can be used to predict mobility of sulfate under a variety of deposition scenarios and soil conditions. If coupled with an appropriate model and with data for cation resupply (exchangeable bases, mineral weathering rates) these models can also predict a time sequence for future acidification and/or a threshold deposition of sulfate which would result in acidification. These models hold great potential for gaining insight into behavior of the ecosystem(s) being modeled, but their quantitative accuracy is uncertain, due in part to problems noted ealier.

No models are currently available to predict nitrate breakthrough, but nutrient cycling data could be used to develop hyptheses on nitrate mobility.

3.4 CATION EXCHANGE PROCESSES

3.4.1 Importance to Direct/Delayed/Capacity Protected Assessment

Cation exchange relationships are a critical factor controlling soil and water acidification. Soil acidification whereby Al^{3+} and H^+ ions displace base cations from the soil exchange complex (i.e., a decrease in base saturation). A substantial decrease in the alkalinity of soil solution can occur if Al^{3+} and H^+ are released into solution from exchange sites in the soil due to base depletion and/or the salt effect; potentially resulting in surface water acidification. Understanding controls on cation exchange in the soil such as base saturation, cation exchange capacity, cation selectivity, concentrations of different cations in input and output solutions, and concentrations of strong and weak acid anions is crucial to assessment of surface water response to acidic deposition.

3.4.2 Chemical theory

This section is excerpted from the keynote address given by J. O. Reuss at the International Workshop on Soil and Water Acidification held in Knoxville, Tennessee in March 1984 and published in Johnson et al. (1985).

3.4.2.1 Capacity-Intensity Concepts

Much of the literature concerning the effect of acid deposition on soils and the soil-mediated effects on surface waters has focused on the capacity of the soil to adsorb proton input. Consider, for example, a system receiving annually 1 m of pH 4.2 rainfall and an equal amount of acidity as dry deposition, for a total of 0.125 eq H^+/m^2. If this input falls on 30 cm of soil with a cation exchange capacity (CEC) of 0.15 eq/kg, a bulk density of 1.2, and a 15% base saturation, a comparison of the pool sizes scaled to the annual input of H^+ would be about as follows:

Annual H^+ input -- 1

Exchangeable base -- 65

Exchange acidity -- 365

Obviously, it would require many decades (centuries in deeper soils) for this input to bring about a significant change in total soil acidity. A significant change in the exchangeable base cation pool due to replacement of acid inputs might occur in a few decades, but this reduction could be mitigated by the release of these cations by weathering processes. The reduction will be further mitigated in some acid soils where the replacement efficiency of the input acidity for exchangeable bases may be substantially less than 1.0.

From considerations such as these, many scientists concluded that soil effects due to acid deposition or soil-mediated effects on surface water are likely to occur only on soils with very low CEC and, therefore, on soils that are highly susceptible to changes in base saturation due to cation loss. However, the capacity effects due to these changes in pool size are not the only manifestation of acid deposition inputs. Changes in soil solution composition that may have a profound effect both on terrestrial ecosystems and on surface and groundwater quality may occur without significant changes in these pool sizes. It is on these so-called intensity factors that we will focus here.

3.4.2.2 The CO_2-HCO_3^- System

While the overall importance of the CO_2-HCO_3^- equilibrium in determining the properties of both soil solutions and surface waters is well known, some of the implications, particularly the role of CO_2 partial pressure (pCO_2) in determining the alkalinity of the drainage water, are often neglected. In acid soils we can neglect the CO_3^{2-} ion so that the reaction can be written as

$$CO_2 + H_2O = H^+ + HCO_3^- . \qquad (1)$$

From this reaction we obtain the equilibrium expression,

$$(H^+)\ (HCO_3^-) = K_c \cdot pCO_2, \qquad (2)$$

where the material in parentheses refers to activities (or partial pressure in the case of pCO_2). If the concentrations are in microequivalents per liter (for our purposes, concentrations and activities may be taken as equal) and the CO_2 in percent, K_c will be about 150. From Eq. 2 we find that at 0.03, 0.3, and 3% CO_2 the product $[(H^+)\ (HCO_3^-)]$ is equal to 4.5, 45, and 450, respectively. In pure water a tenfold increase in CO_2 results in the product of H^+ and HCO_3^- increasing by a factor of 10 (i.e., 3.16) (Table A.3.2). As a result, increasing CO_2 from 0.03% (near atmospheric) to 0.3% decreases pH from 5.67 to 5.17, while at 3% the pH will be 4.67. In pure water the H^+ and HCO_3 concentrations are equal and the alkalinity, defined here as

$$\text{alkalinity} = (HCO_3^-) + (OH^-) - (H^+), \qquad (3)$$

remains zero at all CO_2 levels.

Acid soils are buffered by internal processes, and pH changes with varying CO_2 partial pressures are usually small. Because the product $(H^+) \cdot (HCO_3^-)$ must increase with the CO_2 partial pressure (Eq. 3), and (H^+) is fixed by soil processes, the response to changing CO_2 levels in the soil is mostly in the HCO_3^- concentration, and thus is reflected in the alkalinity of the soil solutions. This is illustrated in Table A.3.2 (lines 4-12). For example, at

Table A.3.2. The effect of pCO_2 on pH, H^+, and HCO_3^- in pure waters and in soil solutions buffered by internal soil processes.

				H^+	HCO_3^-	Alkalinity
	CO_2	$K(CO_2)_g$	pH	(ueq/l)		
Pure water						
1	0.03	4.5	5.67	2.1	2.1	0
2	0.30	45	5.17	6.7	6.7	0
3	3.0	450	4.67	21.2	21.2	0
Soil solutions (buffered)						
4	0.03	4.5	5.67	2.1	2.1	0
5	0.30	45	5.67	2.1	21.2	10.1
6	3.0	450	5.67	2.1	212	0
7	0.03	4.5	5.17	6.7	0.67	-6.0
8	0.30	45	5.17	6.7	6.7	0
9	3.0	450	5.17	6.7	67.2	60.5
10	0.03	4.5	4.67	21.2	0.21	-21.0
11	0.30	45	4.67	21.2	2.1	-19.1
12	3.0	450	4.67	21.2	21.2	0

pH 5.67 and 0.03% CO_2, the H^+ and HCO_3^- concentrations are both 2.1 ueq/l (the same as in water), and the alkalinity is zero. However, increasing CO_2 to 0.3 and 3% increases the alkalinity of the soil solution to 19.1 and 210 ueq/l, respectively. Increasing CO_2 would have no effect on the alkalinity of water not buffered by soil processes.

A soil solution at pH 5.67 will have positive alkalinity if the CO_2 content of the soil gases is above 0.03%. At a solution pH of 5.17 the alkalinity will be positive above 0.3% CO_2, and at pH 4.67 it will be positive above 3%. In this alkalinity-generating process, equal amounts of H^+ and HCO_3^- are formed (Eq. 1), but the HCO_3^- concentration increases while the H^+ is held constant by soil buffering. We may think of the H^+ as being consumed in the dissolution of soil minerals, bringing Al^{3+} into solution. The Al^{3+} then displaces cations such as Ca^{2+}, Mg^{2+}, and K^+ from the ion exchange complex. The net effect is the formation of bicarbonates of these cations (i.e., alkalinity).

The changes in alkalinity brought about in the soil solution by variations in soil pCO_2 can drastically affect the pH of the drainage water. The relationship between alkalinity and pH in water that is not in contact with soil processes, as derived from Eqs. 1 and 2, is shown in Figure A.3.2. The pH 5.17 soil solution (lines 7-9, Table A.3.2) at CO_2 levels of 0.03, 0.3, and 3% has an alkalinity of -6, 0, and 60.5 ueq/l, respectively. When this water equilibrates with atmospheric CO_2 (0.03%), the pH will be 5.17 if the soil CO_2 is 0.03%, 5.67 at 0.3% CO_2, and 7.1 at 3% CO_2. Thus at a soil solution pH of 5.17 the drainage water pH would vary by nearly 1.9 units simply by varying soil CO_2 over a range that may commonly be found in the soil.

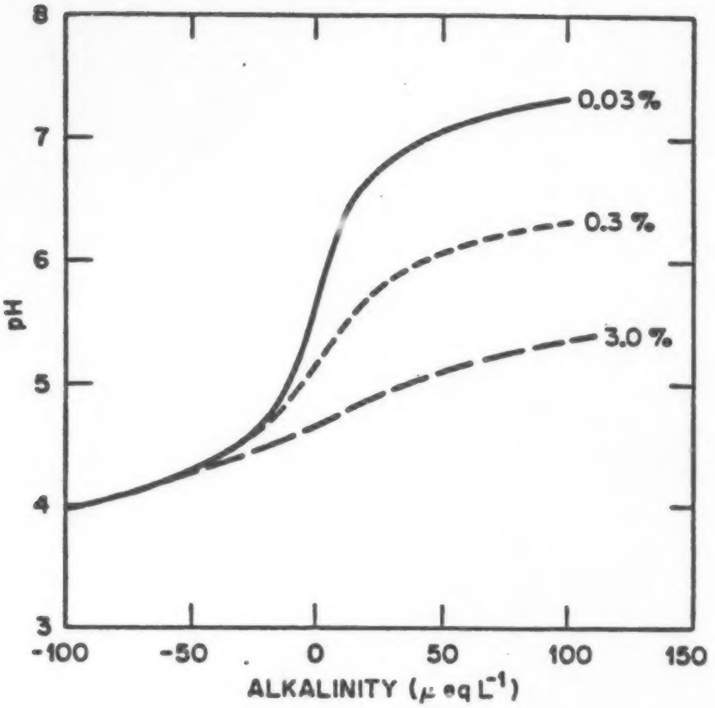


Figure A.3.2. The relationship between the pH and alkalinity of water at 0.03, 0.3, and 3% CO_2.

3.4.2.3 Soil-Solution Equilibria

When an acid forest soil is subjected to acid deposition, the concentration of the strong acid anion (SO_4^{2-}, and in some cases NO_3^-) will increase. In most acid soils the natural concentrations of these anions are very low; a typical value for SO_4^{2-} might be 20 ueq/l. The HCO_3^- is also low due to the nature of the CO_2-HCO_3^--H^+ equilibria described above (e.g., at pH 4.67 and 3% CO_2 the concentration of HCO_3^- will be about 20 ueq/l). Although organic anions can be an important constituent of soil solutions and drainage waters, one of the characteristics of acid forest soils is low anion concentration. When such soils are subjected to acid deposition the increase in SO_4^{2-} concentration can be very significant, typically in the range of 100 to 300 ueq/l. (The time required for this increase in SO_4^{2-} can vary markedly; high-sulfate-adsorbing soils may not come into SO_4^{2-} equilibrium for decades.) This increase in anion concentration can have a very important influence on the cation composition. Not only will the total cation concentration in solution increase to maintain charge balance, but the relative amounts will also change. The most important of these changes involves the H^+, Ca^{2+}, and Al^{3+} ions (we will use Ca as a proxy for both Ca and Mg in this discussion). These responses can be described by the use of three familiar relationships. The first is the relationship between Al^{3+} and H^+:

$$(Al^{3+}) = K_a(H^+)^3, \qquad (4)$$

i.e., the activity of the Al^{3+} ion is proportional to the third power of the H^+ activity or, in negative logarithm form,

$$3\ pH - pAl = K_A. \qquad (5)$$

Values of K_A in the soil may range from 7.0 or less to near 10. Useful reference points are the values of 8.04 and 9.66 given by Lindsay (1979) for gibbsite and amorphous $Al(OH)_3$, respectively. A plot of this relationship for a representative set of K_A values is shown in Figure A.3.3. The implications of the shape of these curves are two-fold. First, if the value of K_A is high the system is highly buffered. For example, if K_A is 9.5 the H^+ concentration is unlikely to exceed about 30 ueq/l (pH 4.5), as any further H^+ will only result in increased Al^{3+} in solution. Second, as shown by the upward curvature of the lines, increasing anion concentrations will result in increases in total cations and in the proportion of Al^{3+} relative to H^+. This consequence can be stated as a general principle, i.e., increasing solution concentration will increase the proportion of the cations with the higher valence.

The second relationship is that between Ca^{2+} and Al^{3+}, which is described below using the equation of Gaines and Thomas (1953):

$$\frac{(Al^{3+})^2}{(Ca^{2+})^3} \cdot K_g = \frac{(AlX)^2}{(CaX)^3} \qquad (6)$$

The parentheses denote activities in the solution phase, K_g is the ion exchange constant that reflects the thermodynamic properties of the exchanger, and CaX and AlX are the fractions of the total exchange sites occupied by the Ca^{2+} and Al^{3+} ions, respectively. Equation 6 states that the activity of Al^{3+} in solution is proportional to the 3/2 power of the Ca^{2+} activity, i.e.,

$$(Al^{3+}) = K_B(Ca^{2+})^{3/2} \qquad (7)$$

The proportionality constant K_B is a function of the degree of saturation of Ca and Al and of the constant K_b (Eq. 6). These relationships tell us that if the solution concentration increases due to increased sulfate or nitrate from acid deposition, the $Al^{3+}:Ca^{2+}$ ratio in solution will increase so that the activity of Al^{3+} remains proportional to the 3/2 power of the Ca^{2+} activity (Figure A.3.3). Again, an increase in solution concentration results in a shift toward the ion of higher valence. This is an intensity response and occurs immediately as the concentration changes.

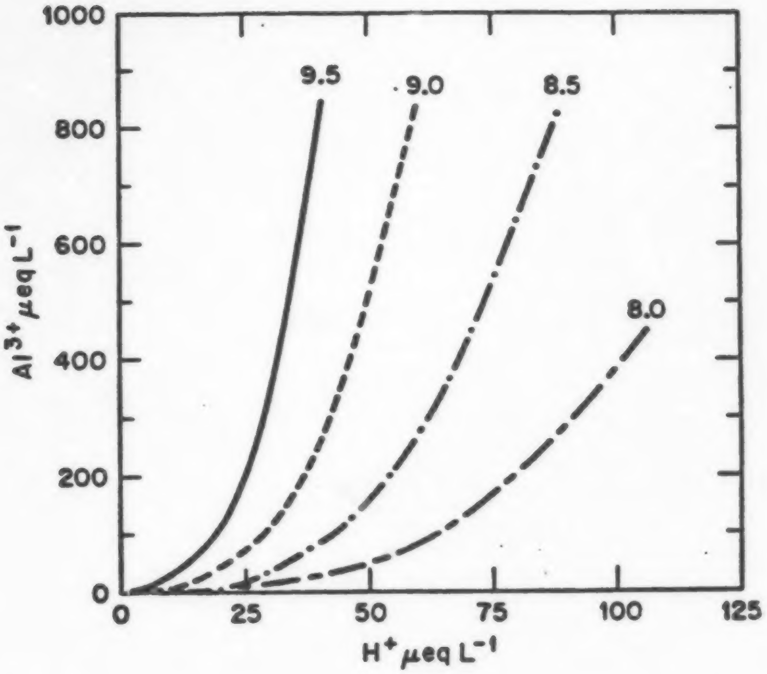


Figure A.3.3. The relationship between the Al^{3+} and H^+, assuming 3 pH - pAl values in the range of 8.0 to 9.5. The activity coefficients are assumed to be 0.96 for H^+ and 0.70 for Al^{3+}.

The lines in the plot of Al^{3+} vs Ca^{2+} (Figure A.3.4) also curve upward, due to an increase in the fraction of Al^{3+} as the total concentration increases. For the K_g value used to construct Figure A.3.4, this curvature increases markedly as the fraction of exchange sites occupied by Ca is reduced below about 0.2. The effect of increasing values of K_g is similar to that of increasing Ca saturation. Thus, increasing K_g has the effect of decreasing the Ca saturation at which the change in the $Al^{3+}:Ca^{2+}$ ratio in solution due to higher concentration becomes significant.

While the effect of an increase in solution concentration due to acid deposition will be a higher proportion of Al^{3+} in solution relative to Ca^{2+} (actually relative to all mono- or divalent cations), the total amount of all ions in solution will increase. Thus, the export of Ca^{2+} is accelerated, even though the $Al^{3+}:Ca^{2+}$ ratio is increased. If the exchangeable Ca pool is depleted due to increased Ca loss over time, the Ca saturation will be reduced and the proportion of Al^{3+} in solution will be further increased.

The third relationship is that between Ca^{2+} and H^+. Combining Eqs. 4 and 6 we obtain the rather formidable-appearing Eq. 8,

$$(Ca^{2+}) = \frac{K_a^{2/3}\, K_g^{1/3}\, CaX}{(AlX)^{2/3}} \qquad (8)$$

This is more familiar to soil scientists in the form,

$$pH - 1/2\ pCa = K_L. \qquad (9)$$

where K_L is the well-known "lime potential." Equation 8 simply states that in the soil solution the Ca^{2+} activity is proportional to the square of the H^+ activity, and that the proportionality is determined by the Al^{3+}-H^+ proportionality constant (K_a), the ion exchange constant (K_g), and the fraction of exchange sites occupied by Ca and Al. Figure A.3.5 shows the H^+-Ca^{2+} relation-

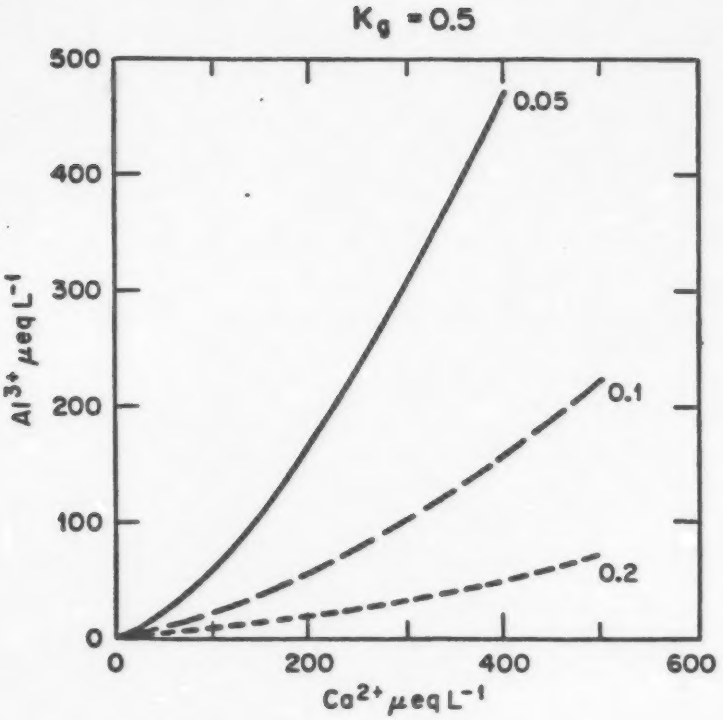


Figure A.3.4. The relationship between the Al^{3+} and Ca^{2+} in soil solution, with the fraction of the exchange sites occupied by Ca^{2+} in the range of 0.05 to 0.20. Log of the Gaines-Thomas exchange coefficient is 0.5 and the activities of Ca^{2+} and Al^{3+} are 0.85 and 0.70, respectively.

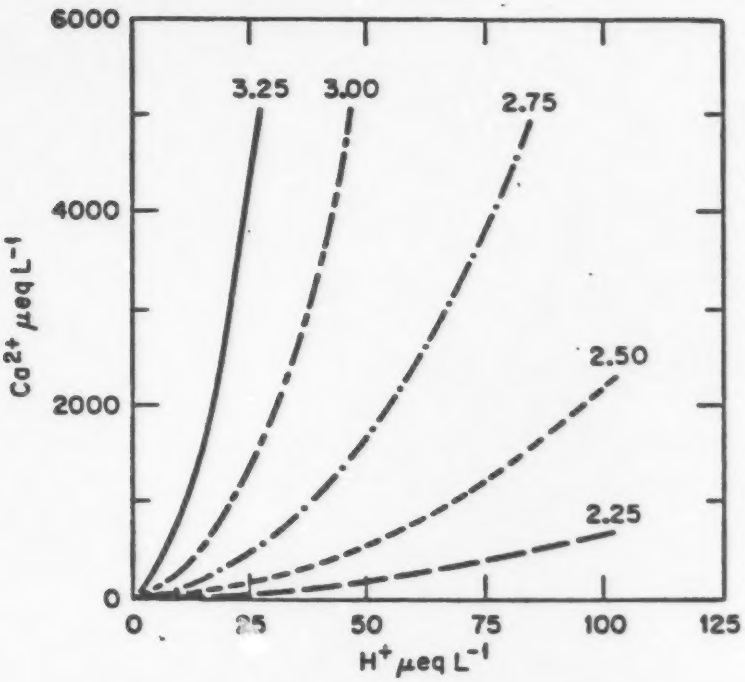


Figure A.3.5. The relationship between the Ca^{2+} and H^{+} in soil solution for lime potential values in the range of 2.25 and 3.25. Calculations assume activity coefficients of 0.96 and 0.85 for H^{+} and Ca^{2+}, respectively.

ship in soil solutions of varying lime potential. The response of the system to increased solution concentrations from acid deposition inputs is again to increase the proportion of Ca^{2+} (i.e., the ion of higher valence) (Figure A.3.5). This figure serves to illustrate the concept of ion exchange buffering. For example, at a lime potential of 3.00, a soil solution pH of 4.3 could only be attained if the Ca concentration were about 1000 ueq/l. As Ca saturation is reduced the lime potential decreases, allowing pH to decrease. Eventually, the pH decrease will be buffered by bringing Al^{3+} into solution (Figure A.3.3) and the pH at which this Al^{3+} buffering occurs will be determined by K_A.

One of the problems with using Eq. 6 is that the ion exchange constant (K_g) is difficult to measure. However, if the solubility of Al^{3+} (K_a or K_A), the degree of Ca and Al saturation, and the lime potential are known, K_g can be calculated by rearranging Eq. 8.

3.4.2.4 Conclusions

It is a relatively simple matter to combine the relationships in Eqs. 2, 4, and 6 with the charge balance requirement to obtain a set of simultaneous equations such that if the various constants and the Ca and Al saturation of the exchange complex are known, the composition of the major cations in solution can be calculated for any combination of anion strength and pCO_2. Additional ions can be included using similar relationships. Several current models are based on similar concepts (Reuss, 1980; Christophersen et al., 1982; Chen et al., 1983). Calculations of this type provide a quantification of the "salt effect" mechanism proposed by Seip (1980). The results indicate that in some low base saturation soils the increase in the anion concentration in solution due to acid deposition inputs may cause a significant increase in the Al^{3+} concentration in the soil solution.

The increase in Al can, under certain conditions, have profound implications for both the plant component of the ecosystem and the quality of the drainage water. The fact that Al^{3+} is toxic to many plants is well known. Unfortunately, the levels at which various forest ecosystems will show significant effects are not well established. The Al^{3+} concentration of the drainage waters is also critical. Within the pH range critical to many aquatic species, Al^{3+} effectively acts as an acid. Thus, the alkalinity of the water (Eq. 3) can be reduced by either H^+ or Al^{3+}. Soil solutions with a low but positive alkalinity may develop negative alkalinity, resulting in a substantial depression in pH of the drainage water. This depression may occur as a direct result of the acid deposition input without the necessity for a reduction in base cation status. In other cases, Al^{3+} will not be significantly increased unless base saturation is reduced by cation export. Soils with a large reservoir of base cations, or those that release substantial cations as a result of mineral weathering processes, may not develop increased Al^{3+} concentrations, even under prolonged exposure to acid deposition.

3.4.3 Measurement

Cation exchange processes *per se* are not generally measured directly, but the results of cation exchange can be measured or inferred by observing changes in dissolved cation concentrations in water as it moves through the soil, or more commonly, by measuring the exchangeable bases, exchangeable acidity, and cation exchange capacity of the soil, from which can be calculated the base saturation of the soil. Several different procedures for extracting cations from soils have been used, each giving different results, and causing confusion in interpretation of data.

Extraction with 1.0 N NH_4OAc buffered at pH 7 has been the standard method of the SCS (USDA, 1984). Values obtained are quite different from extractions with unbuffered 1.0 N NH_4Cl (USDA, 1984), which is presumed to be a better index of cation exchange relationships at the field pH of the soil. Exchangeable acidity has commonly been measured with $BaCl_2$-TEA, pH 8.2 (NCASI, 1983) and 1.0 N KCl (Thomas, 1982).

The equilibrium models being considered for making predictions of soil and water acidification require measurements of exchangeable base cations, acidity, total CEC, and base saturation at field pH. Data from the pilot soil survey are being used to evaluate whether there is a strong relationship between buffered extractant values and values reflecting field pH. A sensitivity analysis of the models should be carried out to determine how significant the uncertainty in the relationship is to model predictions.

3.4.4 Reliability of Measurements

There are two sources of uncertainty in measurements of soil properties, soil spatial heterogeneity and variability in analysis of the soils. The former is generally accounted for in published data by specifying a range of values for the soil kind and horizon, for example in soil survey reports or the Soils-5 database. Any given pedon meeting the description of the soil kind is likely to fall within the range of values for the parameter of interest. Uncertainty in laboratory analysis of soils is discussed in Cronce (1982), the Northeast Soil Characterization Study. An interlaboratory comparison of soil analyses will also be available from the pilot soil survey.

The question of adequacy of the data for regional assessment purposes is not so much reliability of the published data, but rather where within the range of values the soil in question lies, and whether this varies as much within a watershed or region as it does between regions. If the range is too wide to provide useful model predictions or if there is systematic difference between regions in where the actual values fall within the published range, then the published data is not useful for this assessment purpose. It may be possible to test this using the pilot soil survey data.

3.4.5 Expected Range and Regional Distribution

The range and regional distribution for BS, exchangeable bases, and CEC (determined in NH_4OAc buffered at pH 7) is shown in Section 2.3.2, Figures A.2.3, A.2.4, and A.2.5. At field pH the CEC values would be lower and the BS values higher.

3.4.6 Threshold Values for Categorizing Direct/Delayed/Capacity Protected Watersheds

Threshold values for pH-7 buffered data have not been determined because the predictive models use equilibrium relationships dependent on data for field pH conditions. The high-moderate-low categories used in Figure A.2.6 (Section 2.3.2) were based on qualitative criteria discussed in Olson et al. (1982) and Seip (1980). They do not necessarily directly correspond to direct/delayed/capacity-protected categories. Threshold values for the field-pH data have also yet to be determined, although Reuss and Johnson (1985) have suggested 15-20% BS as an upper limit for sensitive soils. They point out, however, that the physical-chemical mechanism is dependent on several factors (pCO_2, aluminum solubility, cation exchange selectivity, and base saturation), none of which are independent of the others. A single sensitivity threshold, therefore, is impossible to assign to any one parameter such as base saturation. Little or no data is available for pCO_2, aluminum solubility, and cation exchange selectivity for soils on a site-specific or regional basis.

3.5 CATION WITHDRAWAL AND REDISTRIBUTION BY VEGETATION

3.5.1 Importance to Direct/Delayed/Capacity Protected Assessment

Soils can be acidified by plant uptake of base cations in excess of anions (resulting in H^+ release from roots to maintain charge balance). This may be of importance to the direct/delayed issue, since one can envision a scenario in which a surface water is acidified as the soil is acidified by plant uptake even under constant atmospheric loading.

3.5.2 Chemical Theory

Plant uptake is acidifying to the rhizosphere if the sum of base cation uptake exceeds the sum of non-bicarbonate anion uptake (Nye, 1981). In this case, plants release H^+ or take up HCO_3^- (which results in dissociation of H_2CO_3) to H^+ + HCO_3^- and is equally acidifying). The form in which N is taken up -- $NH_4^=$ or NO_3^- is of crucial importance to the charge balance of roots (and, consequently, the acidification of the rhizosphere) since uptake of the other major nutrient anions (PO_3^{3-} and SO_4^{2-}) normally cannot balance base cation uptake. Unfortunately, the form of N uptake under field conditions is seldom known (although frequently guessed at), making estimates of rhizosphere acidification due to plant uptake extremely uncertain.

3.5.3 Sources and Sinks

On a whole-soil basis, it can be shown that N mineralization followed by uptake has no net effect on H^+ production. That is, the H^+ consumed during N mineralization of organic N to NH_4+ is offset by H+ produced during NH_4+

uptake. If nitrification occurs, there is still an H^+ balance if NO_3^- is taken up [i.e., 2 H^+ produced during nitrification are balanced by one H^+ consumed during N mineralization and one H^+ consumed during NO_3 uptake (Reuss, 1977; Ulrich, 1980)]. Another way of looking at it is that the transformation from organic N (in soil) to organic N (in plants) has no net effect on H^+ production, and the same principle applies to transformations of organic P, S, Ca, K, and Mg (Ulrich, 1980). Thus the net acidifying or alkalizing effects of plant uptake on whole-soil (i.e., not rhizosphere) acidity are due to the uptake of nutrient ions from inorganic sources, i.e., atmospheric deposition and soil exchange sites.

3.5.4 Factors Affecting Acidification by Plant Uptake

Factors affecting the acidification due to plant uptake are atmospheric inputs of nutrients, including forms of N (NH_4^+ vs NO_3^-) (as discussed above), the amount of nutrient required by the plant (especially Ca^{2+}), and the rate of soil weathering (discussed later). Species that accumulate large amounts of Ca, such as oaks, hickories (Johnson *et al.*, 1982) aspen and white spruce (Alban, 1982) are more likely to have an acidifying effect than species which accumulate less Ca (e.g., pines).

3.5.5 Effects of Acidic Deposition

Ulrich (1984) argues that the rhizosphere is the zone at which much of the acidifying effects of acid deposition are ultimately manifested. This argument is based upon the assumption that acid deposition causes accelerated foliar cation leaching which in turn causes accelerated cation uptake which in turn causes accelerated H^+ release from roots.

It should be noted, however, that root turnover and, consequently, rhizosphere turnover, are very rapid (Harris et al., 1977) and thus one could argue that whole-soil acidification calculations are most meaningful for long-term considerations of soil acidification.

3.5.6 Measurement of Effects of Plant Uptake on Soil Acidification

A nutrient cycling approach is necessary to estimate the potential effects of plant uptake on soil acidification. From nutrient cycling data, one can estimate the net annual increment of nutrients in biomass, compare this with atmospheric inputs, and estimate from that difference how much (if any) of the biomass increment must come from soil sources. If it is further assumed that soil sources of base cations for biomass increment are exchange sites (not organic), then an ecosystem-level estimate of potential soil acidification due to plant uptake can be made.

One way to avoid the uncertainties associated with form of N uptake and sources of nutrients for uptake is to consider only the accumulation of base cations in vegetation and the potential depletion of exchangeable base cations as a result. Alban (1982) found an apparent effect of forest Ca^{2+} cycling patterns on soil exchangeable Ca^{2+} and pH. High rates of Ca^{2+} uptake and cycling by aspen and white spruce stands had apparently caused a depletion of exchangeable Ca^{2+} (and a lowering of pH) in mineral soils and an enrichment of exchangeable Ca^{2+} (and an increase in pH) in surface soils over a 40-year-period in glacial outwash soils in Minnesota. In contrast, red and jack pine forests, which took up and cycled much less Ca^{2+}, had more acid litter but less acid subsoil than the aspen or spruce stands.

3.5.7 Reliability of Measurements

Uncertainties associated with nutrient cycling data are considerable. This is especially true for net nutrient increment in biomass, since annual or even periodic destructive sampling of forest woody matter is usually infeasible. Normally, biomass is estimated from regression equations using diameter and possibly also height as the independent variables and nutrient increment is estimated from selected analyses of subsampled tissues.

Measuring changes in soils is even more difficult due to the inherent variability. Long-term studies (10-20 years at least) are required and one must be satisfied with being able only to see relatively large changes over long periods (e.g., 40 years as in Alban's study).

3.5.8 Expected Range and Regional Distribution

As mentioned above, the acidifying potential of tree uptake is related to amounts of base cations (especially Ca^{2+}) which are taken up. There appear to be certain species or genera which accumulate Ca^{2+} and it may be possible to plot the distribution of Ca^{2+} accumulating forest types on a regional scale to gain a qualitative insight into the regional distribution of this effect.

3.5.9 Threshold Values for Categorizing Direct/Delayed/Capacity Protected Watersheds

Due to the numerical uncertainties described in Section 2.5.6, it is not possible to address this question. Assessments must be limited to a qualtitative, not a quantitative analysis.

3.6 CATION REPLENISHMENT

3.6.1 Importance to Direct/Delayed/Capacity Protected Assessment

Replenishment of base cations to soil exchange sites is the process that prevents or delays natural and anthropogenic acidification of soils. There are two possible net sources of base cations to the exchange complex in soils; mineral weathering and atmospheric inputs. If additions to exchange sites from mineral weathering and the atmosphere balance the leaching of base cations by natural or anthropogenic acid anions, the soil will not acidify. If mineral weathering plus atmospheric inputs do not keep pace with base cation leaching, the base saturation of the soil will decline. Assessing the rate of decline or length of delay before acidification of soils and surface waters takes place is dependent on knowing the rate of cation replenishment to soil exchange sites; i.e., knowing weathering rates and atmospheric input rates.

Weathering also occurs in regolith, till, or unconsolidated parent material below the rooting zone. Cation exchange capacity is generally much lower in those materials, but they are often quite thick, and the relatively slow-moving water through such materials (that appears as baseflow to surface waters) generally develops high alkalinity.

An overview of the factors affecting atmospheric deposition and problems with measuring it was given in Sections 2.2.1 and 2.2.2, and the state of our knowledge summarized again in the introduction to Section 3. It will not be discussed further here except to reiterate that large errors of measurement of wet deposition may occur, and nonmeasurement of dry deposition may substantially underestimate the total inputs to a region. Also, it is unknown how inputs vary among watersheds within a region, for example, between slopes of different elevation or aspect, or areas with different canopy cover types. This (unknown) uncertainty must be factored into estimates of uncertainty of the direct/delayed/capacity protected assessment, and some testing should be done in the field to put some bounds on the uncertainty.

3.6.2 Theory and Measurement of Weathering Rates

The primary mineralogy of most igneous and metamorphoric rocks reflects the conditions of high temperature and pressure where the minerals were formed beneath the earth's surface. The weathering process is a readjustment the minerals make toward a new chemical equilibrium reflecting the environmental conditions at the earth's surface, where lower temperatures and pressures, the presence of water, various organic and inorganic acids, and numerous other compounds occur. Sedimentary rocks may be composed of materials previously weathered and eroded, such as sands, silts, and clays, or they may be formed from chemical precipitates, such as $CaCO_3$ (limestone). The former are generally relatively resistant to further weathering, having previously been through at least one weathering and erosion cycle. The chemical precipitates are very unstable in humid climates.

The weathering processes, reactions, and products for the common rock-forming minerals have been summarized in numerous publications including Loughnan (1969), Carroll (1970), Bache (1983), and Johnson (1984), and will not be repeated here. Studies of the relative rates of these processes for individual minerals under certain, usually controlled, conditions are scattered throughout the literature. The minerals can be ranked into stability series, as has been done by Goldich (1938). Considering the mineral composition of different rock types, rocks can also be ranked according to weatherability, and areas of different potential weathering rates mapped, as has been done by Norton (1980). These techniques lead to an ability to assess relative weathering rates for different minerals or rock types within a region or between regions, but gives little information on absolute rates of weathering, or the amounts of individual cations that are needed as input to the predictive models for assessing rates of soil base cation depletion.

Clayton (1979) summarized the methods that have been used to study weathering rates, grouping them into four categories: (1) descriptive field studies of weathering for Quaternary stratigraphic research; (2) watershed level studies utilizing mass balance techniques for determining nutrient budgets or chemical denudation rates; (3) tension lysimeter studies for determining nutrient budgets; and (4) laboratory studies of mineral weathering. He discussed the techniques, results, advantages, and drawbacks of several example studies that used each method. His conclusions are presented below.

"Figures on absolute rates of rock weathering are not common, but geology and soils literature can provide data from a variety of regions and climates. Predicting nutrient release from available rock weathering rates is a problem of greater concern.

"Rock weathering rates based upon primary mineral grain etching and time of disappearance of particular minerals in soil must be considered of limited value because of the long time periods (10^4 to 10^5 years) before recognizable weathering takes place. This is the case even for relatively easily weathered minerals of small particle size. Known climatic fluctuations over these time periods suggest that predictions of current weathering rates based upon long-term mineral grain etching are unlikely to be accurate. The one exception may be weathering in soils of calcic plaioclase, which has been shown to weather extensively in 10^4 years in both central Europe and the British West Indies. Computing Ca release from this rate of plagioclase weathering, though gross, may be considered a somewhat reliable best estimate when no other data are available.

"Estimates of nutrient release based upon thickness of weathering rinds present similar problems to estimates based upon mineral grain etching. Although the zone of weathering may be accurately portrayed by a suitable sample of rind thickness measurements, we know little about the actual amount of material released. These estimates will improve when we have data on bulk densities and mineralogical changes during rind formation. The potential effects of climatic change over long periods of time necessitate caution in using weathering rind data on deposits older than 10,000 years.

"The effects of cold climates on rate of chemical weathering may be more complicated than we previously thought. We generally expect the rate to go down as temperature decreases; in harsh glacial environments, the rate of chemical weathering has been considered to be very low. Reynolds and Johnson (1972) found chemical denudation rates from waters draining a glacier in the northern Cascade Mountains to be three times the world average for temperate basins. Apparently the low temperature effects were offset by comminution of rock by ice grinding, which accelerated chemical weathering in this study. Birkeland (1973) also indicated that rates of chemical weathering do not decrease in the alpine climate above tree line in the Rocky Mountains of Colorado.

"The studies emphasize the fact that relationships between chemical weathering and climatic regime are not well understood. Differences in weathering rates between cold and temperate climates may be quite small.

"Mass balance nutrient studies provide the best estimates of nutrient release from rock weathering, but the published studies vary widely in their approach and attention to detail. The most complete studies include accurate assessment of nutrient sources and sinks and of proposed chemical reactions for weathering of minerals. Such studies require sound data on net biomass accumulations of nutrients, nutrient gains to the soil, and consideration of differential weathering rates of minerals, in addition to data on precipitation inputs and losses in water. The complex geochemistry of weathering reactions coupled with the complex cycling between soil and plants indicates that transfer rates of nutrients between all points in the biogeochemical system must be considered to quantify rock weathering rates. Of the studies reviewed in this paper, those by Marchard (1974), Cleaves _et al_. (1970, 1974), and Likens _et al_. (1977) most completely fit these requirements.

"The principal drawbacks to mass balance studies of nutrient flows are the time and costs involved. Long-term hydrologic and meteorologic data are required for watershed-level studies and such data are costly. Temporal variations in chemical fluxes are generally more stable than hydrologic and climatic regimes, but relationships between water yields and chemical fluxes must be established. This involves careful sampling of extreme events.

"Similar problems exist for lysimeter level studies. Grier and Cole (1972) pointed out the magnitude of difference in chemical influx from precipitation from year to year. Annual variations in elemental loss below the rooting zone are similar to variations observed in stream water. The credibility of lysimeter estimates of nutrient release is also enhanced by long-term studies.

"Laboratory studies of mineral weathering require much less time and are less costly as well. Laboratory research does not suffer at the mercy of climatic irregularities, and sampling is greatly simplified. The principal drawback to laboratory simulations of weathering is a lack of demonstrable extrapolation to the field. Laboratory simulations of weathering that best mimic field weathering include judicious use of acids and organic components that are found naturally in soils. Simulating microbiological influences is more difficult, but not impossible. As laboratory studies become more common, comparisons with field research should provide a basis for judging their accuracy" (Clayton, 1979).

3.6.3 Adequacy of Data for Direct/Delayed/Capacity-Protected Assessment

Enough data on relative weathering rates exists to predict the relative differences in weathering of different rock types, as has been done by Norton (1980). The data do not exist with which to predict the absolute amounts of total base cations or individual base cations that may be made available to replenish cation exchange sites, on a watershed or regional basis.

3.7 IN-STREAM AND IN-LAKE PROCESSES

3.7.1 Importance to Direct/Delayed/Capacity-Protected Assessment

The question being addressed in this section on in-stream and in-lake processes is: "What happens when acidic deposition, either indirectly from the terrestrial landscape or directly from the atmosphere, reaches aquatic systems?" Perennial streams and lakes are both (1) receptors of soluble and particulate materials transported from the surrounding watershed and deposited directly from the atmosphere, and (2) biogeochemical reactors that transform and retain these materials. The linkage between terrestrial and aquatic ecosystems thus includes not only the flux of alkalinity, acidity, and associated anions and cations from the terrestrial to the aquatic system, but also the internal hydrologic, geochemical, and biological processes that mediate the concentration and flux of these and other materials within surface waters.

Although data are very limited on this topic, results suggest that in areas sensitive to acidic deposition, the neutralization of hydrogen ion by within-lake processes can be important and in some watershed-lake systems may be the only significant mechanism for modifying acidic deposition (Cook 1984). Clearly, processes within aquatic systems must be included in any model for categorizing watersheds as direct, delayed, or capacity-protected.

There are three major areas relating to in-stream and in-lake processes that must be considered in order to quantify and predict the response of surface waters to acidic deposition. These are: (1) the role of surface water hydrology in surface water acidification, including the spatial and temporal hydrodynamics that influence the flux of alkalinity and acidity to streams and lakes, and the internal mixing and distribution of these materials within aquatic ecosystems; (2) the quantitative role of internal geochemical processes within the sediments and water column as contributing sources to the acid neutralizing capacity, and acidity, of surface waters; and (3) the quantitative role of biological processes within surface waters and sediments as supplemental sources of the acid neutralizing capacity and acidity in aquatic systems. Categorizing watershed systems as direct, delayed, and capacity-protected will require being able to quantify the direct and indirect effects of acidic deposition on these geochemical and biological processes.

3.7.2 Hydrologic Pathways

The extent to which atmospheric sources contribute to the hydrogen budget of surface waters is determined, in part, by the primary flow paths of water entering streams and lakes. Eilers et al. (1983) report that the susceptibility of lakes in north-central Wisconsin can be judged largely on the basis of their hydrology. They conclude that the most susceptible lakes, those classified as "precipitation dominated," can be identified using watershed-to-lake area ratios and by the presence or absence of surface inlets and outlets. Separating lakes into seepage and drainage categories using these criteria is, however, unlikely to achieve the same result outside this physiographic region. In the Adirondack region, for example, many acidic lakes have surface inlets and outlets (Chen _et al_., 1982), lakes are as susceptible as "precipitation-dominated" systems. Eilers _et al_. (1983) suggest that a more fundamental measure of susceptibility is the lake-groundwater interaction. Groundwater usually is more alkaline than surface runoff and it has a greater potential for generating alkalinity on entering a lake through geochemical and biological interaction with lake sediments. Thus, by quantifying the contribution of groundwater to the water budget of a lake, one will have a measure of a prime factor in the alkalinity supply to a lake.

Although similar analysis of the influence of watershed hydrology on stream acidification has not been reported, the importance of groundwater would be expected to be similar to that for lakes. The proportion of stream runoff derived from groundwater has been shown to be inversely related to the drainage density (total length of all stream segments per drainage basin area) of a watershed (Carlston, 1963; 1966). Thus, as drainage density increases, the contribution of groundwater to stream flow declines due to the lower capacity of the more heavily incised watersheds to retain groundwater. Surface waters draining watersheds with high drainage densities should be more susceptible to acidification from acidic deposition because of the shorter flow paths of water through soil and groundwater and the correspondingly lower contact time of solutes with substrates that neutralize acidity.

Temporal variations in the proportion of stream flow derived from subsurface versus overland flow in watersheds with a low drainage density will also influence the susceptibility of surface waters to acidic deposition. During snowmelts and intense rainstorms, water can enter stream channels without passing through the mineral soil horizons and groundwater where significant buffering can occur. Under such conditions, streams and lakes may undergo temporary increases in acidity due to the overland flow of acidic deposition directly into the stream channel or lake basin.

Dilution, dispersion, and mixing or transport characteristics of streams and lakes are also of prime importance in understanding the response of surface waters to acidic inputs. After water enters a stream channel, there is continuing opportunity for neutralization of acidity by geochemical and biological processes. In undisturbed watersheds, the sites of these neutralizing reactions are primarily in the bottom sediments. The acid-neutralizing capacity of a stream depends on the rate of such reactions (e.g., cation exchange, denitrification, sulfate adsorption) and the extent of mixing of water with alluvial materials in the stream channel, thereby allowing the reactive ions (H^+, $Al(OH)n$, $SO_4{}^{2-}$, $NO_3{}^-$) in solution to contact sediment particles and substrata.

After water enters a lake basin, there is an even greater continuing opportunity than in streams for neutralization of acidity by geochemical and biological processes. Lakes are extremely vulnerable to short-circuiting of inputs in the mixing process because of restrictions of the vertical exchange of water and solutes by the thermocline throughout much of the year. For lakes in regions with snowpack, this short-circuiting may be advantageous during the first snowmelt because the impact of this highly acidic input is minimized by its short retention time within the upper layer of the lake. If this source of acidity mixes with deeper waters or induces the spring overturn (and mixes with the entire lake), it can have a more adverse impact due to its longer-term retention in the lake. On the other hand, if there are significant internal sources of alkalinity within the hypolimnion (i.e., from cation exchange, mineral weathering, and sulfate adsorption in the sediment and from bacterial reduction of sulfate and nitrate in the sediment and water column), mixing of such acidic inputs with the entire lake volume may lessen their impact. Spatial variability in mixing characteristics can also occur as a result of the geometric configuration of the lake, depth restrictions, and spatial variability of forcing mechanisms (e.g., wind, inlet and outlet streams).

As in streams, the dispersion and mixing characteristics of a lake will also affect the supply of strong acid anions (sulfate, nitrate) and hydrogen ions to zones within the lake where the neutralization rate may be greater (e.g., anoxic hypolimnion) . Inasmuch as a supply of nitrate and sulfate is necessary to support dissimilatory nitrate and sulfate reduction (i.e., use of nitrate or sulfate as electron acceptors in the oxidation of organic matter by anaerobic bacteria) these processes may be limited by eddy or molecular diffusion of nitrate and sulfate to the anoxic portions of lakes that do not mix completely. On the other hand, lakes with considerable advective and convective mixing may be limited in their capacity to generate alkalinity due to the presence of oxygen.

Even in well mixed lakes, however, alkalinity can be generated in sediments and transported into the overlying water by molecular diffusion and biological mixing. Pore water pH and alkalinity profiles for a number of acid-sensitive lakes in the Upper Midwest, New York, and Norway reveal alkalinity increases in sediments to as high as 500 ueq/l and pH values as high as 6.5 (Cook, 1984; Cook et al., 1985; Rudd et al., 1985). These increases occur because sediments become anoxic within a few centimeters of the sediment-water interface. Net alkalinity generation of these sediment systems depends upon their ability to retain reduced sulfur and nitrogen compounds. Any oxidation of these reduced species will result in the generation of acidity, thus negating the production of alkalinity. The internal hydrodynamics and mixing characteristics of lakes thus are critical to understanding their internal capacity to neutralize acidity.

3.7.3 Geochemical Processes

The geochemical processes discussed above for soils also occur in stream and lake sediments. These processes can play an important role in determining the rate and extent of surface water acidification or recovery in response to changes in loading of strong acid anions from acidic deposition. Geochemical properties of particular importance in this regard are: (1) cation exchange capacity and selectivity; (2) weathering or solubility of minerals in stream and lake sediments; (3) anion retention or sorption properties; and (4) the salt effect. The quantitative importance of buffering by exchange and weathering processes in stream and lake sediments is poorly understood, and except for a few lakes (Cook, 1984; Goldstein and Gherini, 1984; Cook *et al*., 1985; Schindler *et al*., 1985; Baker, 1984; Wright, 1983; Wright and Johannessen, 1980) it remains to be demonstrated whether sediments are a significant source or a sink for protons in terms of current or projected loading rates of strong acid anions from atmospheric sources.

Prior work on geochemical processes in lake and stream sediments as buffering mechanisms focused primarily on well-buffered systems (e.g., Kennedy, 1965; Toth and Ott, 1970), and similar information for poorly buffered streams and lakes is lacking. Hongve (1978) examined the role of sediment buffering using cores from an acidified lake (pH 5.1). While there was significant buffering by the sediments when the pH of overlying water was reduced to 4.0, the extent to which it resulted from cation exchange versus mineral dissolution is not known. Recent work at the Experimental Lakes Area in Canada, in Florida, and in Wisconsin has demonstrated that geochemical processes in bottom sediments do contribute to the neutralization of acids in some poorly buffered lakes (Schindler et al., 1980; Schindler and Turner, 1982; Cook, 1984; Schiff and Anderson, 1985; Baker, 1984). The contribution of each geochemical process (i.e., cation exchange, mineral weathering, sulfate adsorption) to the buffering capacity of streams and lakes, and the rate of buffering by these geochemical processes relative to the acid loading rate need to be quantified. In particular, the cation exchange capacity and the sulfate adsorption capacity of lake and stream sediments should be quantified in the field to define the buffering capacity of these processes at different loading rates of strong acid anions.

Because the cation exchange rate of the larger sediment particles (sand, gravel) which dominate the bottom sediments in many systems, particularly streams, is relatively slow compared to that of the silt-clay particles (Malcolm and Kennedy, 1970), neutralization of acidity by cation exchange may be limited by the cation exchange rate rather than by the cation exchange capacity. Under such conditions, the neutralization of acidity by cation exchange will depend on the extent and duration of mixing of sediments and water.

Buffering by anion (i.e., sulfate) adsorption by sediments is also dependent on the extent of mixing of sediments and water. Further, this process may increase in importance as a buffering mechanism in response to acid deposition, due to the protonation of hydrous oxides of iron, manganese, and aluminum. The quantitative relationship between sulfate adsorption and sediment protonation thus needs to be tested under field and laboratory conditions.

Inasmuch as desorption of sulfate from stream and lake sediments could affect the recovery rate of aquatic systems upon reduction in strong acid anion loading, the reversibility of sorption processes by sediments must also be quantified. If the rate of sulfate desorption from sediments is relatively rapid, or if adsorption is largely irreversible, the recovery of aquatic systems should be relatively rapid. On the other hand, slow desorption could delay the recovery, due to continual release of sulfate into stream and lake water. At the present time, quantitative information on sulfate adsorption-desorption kinetics by sediments in poorly buffered surface waters is lacking.

The role of mineral weathering of sediments as a geochemical buffering mechanism in surface waters is also incompletely understood because of a lack of information on mineral phases in the sediments and the weathering rate response to pH. Work to date on sediment buffering has not distinguished cation exchange from mineral dissolution. The same two hypothesized mechanisms dealing with the geochemistry of soil-water systems which could explain how acidic deposition causes the acidification of surface waters (i.e., the depletion of base cations on soil exchange sites and the salt effect; see Section 3.4) may also apply to sediment-water systems and, thus, could mediate the rate and extent of acidification of surface waters and their recovery.

It is clear from the above discussions that geochemical characteristics of stream and lake sediments, including cation exchange, cation selectivity, sulfate sorption, mineral weathering, and base saturation, interact in many currently unquantified ways to influence the rate and extent of acidification and the recovery of surface waters.

3.7.4 Biogeochemical Processes

Surface waters are not abiotic reservoirs or conduits through which strong acid anions and associated protons deposited from the atmosphere simply pass affected only by geochemical processes. Rather, they are biologically active systems in which a number of metabolic reactions involving protons occur, including the cycling and transformation of sulfur and nitrogen. These biological reactions include anabolic processes (the formation of organic matter) and catabolic processes (the oxidation of organic matter).

Biological processes, especially those involving the cycling of strong acid anions (SO_4^{2-}, NO_3^-), can mediate the rate and extent of surface water acidification by: (1) consuming protons through assimilatory and dissimilatory nitrate and sulfate reduction in the water column and sediments of surface waters; and (2) releasing protons through the reverse reactions of many of these processes (e.g., oxidation of inorganic and organic sulfur and nitrogen) thus potentially contributing to the acidification of surface waers (Van Breeman _et al_., 1983; 1984). [The assimilatory reduction involves the use of sulfate and nitrate as sulfur and nitrogen sources, respectively, in anabolic processes, whereas dissimilatory reduction involves the use of sulfate and nitrate as electron acceptors in catabolic processes (Figure A.3.6).]

The extent to which these biological processes mediate surface water acidification is dependent on, among other things, the nutrient status of the ecosystem in question. The supply of essential nutrients (e.g., phosphorus, base cations) directly limits anabolic processes, thereby limiting the supply of readily oxidizable autochthonous organic matter for catabolic processes. Any modification of the supply of nutrients by ecosystem acidification will affect the capacity of the metabolic processes to neutralize hydrogen ion. The

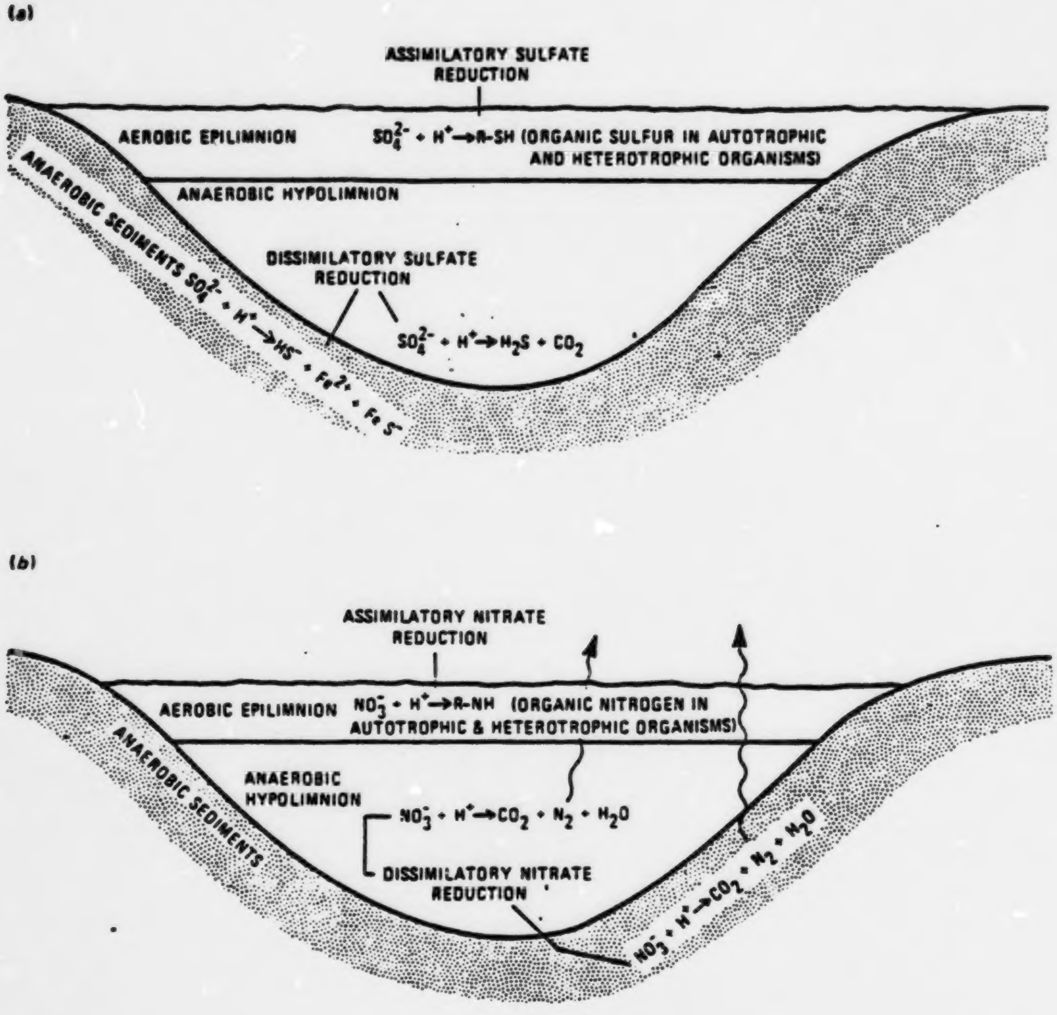
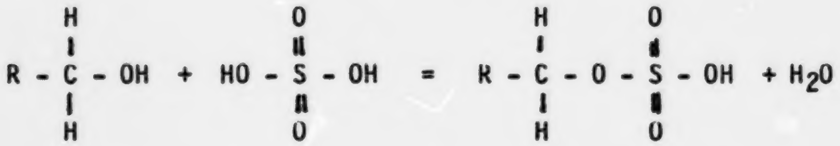

(a)
ASSIMILATORY SULFATE REDUCTION
AEROBIC EPILIMNION
$SO_4^{2-} + H^+ \rightarrow R\text{-}SH$ (ORGANIC SULFUR IN AUTOTROPHIC AND HETEROTROPHIC ORGANISMS)
ANAEROBIC HYPOLIMNION
ANAEROBIC SEDIMENTS $SO_4^{2-} + H^+ \rightarrow HS^- + Fe^{2+} + FeS$
DISSIMILATORY SULFATE REDUCTION
$SO_4^{2-} + H^+ \rightarrow H_2S + CO_2$
(b)
ASSIMILATORY NITRATE REDUCTION
AEROBIC EPILIMNION
$NO_3^- + H^+ \rightarrow R\text{-}NH$ (ORGANIC NITROGEN IN AUTOTROPHIC & HETEROTROPHIC ORGANISMS)
ANAEROBIC HYPOLIMNION
$NO_3^- + H^+ \rightarrow CO_2 + N_2 + H_2O$
DISSIMILATORY NITRATE REDUCTION
ANAEROBIC SEDIMENTS
$NO_3^- + H^+ \rightarrow CO_2 + N_2 + H_2O$

Figure A.3.6. Schematic diagram of alkalinity production by assimilatory and dissimilatory sulfate reduction (a) and nitrate reduction (b) in the aerobic epilimnion and anaerobic hypolimnion and sediments of a lake.

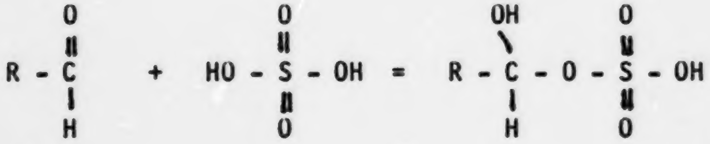
effect of acidification on nutrient supply and net ecosystem production is complex and poorly understood.

3.7.4.1 Sulfur Transformation in Aquatic Ecosystems

Direct Sulfate Assimilation is a process whose role in geochemical cyling of sulfur has not been investigated in any detail in aquatic ecosystems, although, in certain environments, it may be a more common process then previously recognized (Holdren/Mitchell, pers. commun.). Direct assimilation involves the direct incorporation of sulfate into growing biomass. Although details of this reaction are not currently known, two possible pathways might include:



$$R-\overset{H}{\underset{H}{C}}-OH + HO-\overset{O}{\underset{O}{S}}-OH = R-\overset{H}{\underset{H}{C}}-O-\overset{O}{\underset{O}{S}}-OH + H_2O$$



$$R-\overset{O}{\underset{H}{C}} + HO-\overset{O}{\underset{O}{S}}-OH = R-\overset{OH}{\underset{H}{C}}-O-\overset{O}{\underset{O}{S}}-OH$$

Each of these reactions consumes half of an equivalent of acidity for each equivalent of sulfate incorporated. As with the other processes to be discussed, net generation of alkalinity requires that the endproduct, ester sulfates, be removed either to sediments or flushed from the system via stream outflow. Ester sulfate remineralization consumes alkalinity, although, at present, the importance of the role that such reactions play in the sulfur cycle has not been quantified.

Assimilatory sulfate reduction involves the use of sulfate as a sulfur source in anabolic processes. This reaction also consumes hydrogen ion and produces carbon-bonded sulfide:

$$H^+ + SO_4^{2-} \qquad C\text{-}S\text{-}H$$

In order for assimilatory sulfate reduction to contribute to the alkalinity balance for a lake, the carbon-bonded sulfide must be deposited in the sediments through either depositional or diagenetic processes and it must not undergo subsequent reoxidation (the reverse or catabolic reaction). Because of the abundance of sulfate in aquatic ecosystems relative to the growth requirements of most organisms, sulfate is rarely limiting to growth. However, increases in aqueous sulfate concentrations can lead to increased uptake and storage of sulfur by aquatic organisms (Monheim, 1974). Whether this increased uptake contributes to net alkalinity production or simply increases the sulfur cycling rate is not currently known.

Dissimilatory sulfate reduction involves the use of sulfate as an electron acceptor in the anaerobic oxidation of organic matter. The balanced reaction is:

$$2H^+ + SO_4^{2-} + 2CH_2O \qquad H_2S + 2CO_2 + 2H_2O$$

Production of alkalinity depends on the fate of the reduced sulfur. If sulfide becomes exposed to oxygen, it will be oxidized back to sulfate and hydrogen ion, with no net production of alkalinity. Alkalinity will be produced if the H_2S is transported from the sediments or water column into the atmosphere or if the sulfide is permanently sequestered in the sediments. The loss of H_2S to the atmosphere by gas exchange is not a viable source of alkalinity because gas exchange is typically slower (Emerson, 1975; Hesslein *et al*., 1980) than chemical oxidation of H_2S (Chen and Morris, 1972).

The alkalinity produced by sulfate reduction is preserved if the sulfide is sequestered as amorphous iron sulfide (FeS) or as pyrite (FeS_2):

$$9\ CH_2O + 4\ SO_4^{=} + 4\ FeOOH = 4\ FeS + 9\ HCO_3^{-} + H^{+} \tag{a}$$

$$15\ CH_2O + 8\ SO_4^{=} = 4\ FeOOH + H^{+} + 4\ FeS_2 + 15\ HCO_3^{-} + 10\ H_2O \tag{b}$$

In either case one microequivalent of alkalinity is produced for each microequivalent of sulfate reduced. As in assimilatory sulfate reduction, the net production of alkalinity from these reactions ultimately depends on the ability of sediments to store reduced sulfur compounds.

The production of alkalinity by dissimilatory sulfate reduction is dependent on: (1) the absence of oxygen in either the water column or the sediments; (2) the supply of readily metabolizable organic matter; (3) the supply of reactive iron; (4) the supply of sulfate; and (5) the ability of sediments to preserve iron sulfide minerals. Although our knowledge regarding the relative importance of these factors on the rates of alkalinity production is incomplete, recent work has shed some light on them.

Dissimilatory sulfate reduction requires a supply of readily metabolizable organic substrate. Sources for this may be either autochthonous or allochthonous (Schindler, 1985), although allochthonous sources are believed to contribute predominantly refractory humic and fulvic substances to aquatic ecosystems. As a result, microbial decomposition rates (and hence microbial sulfate reduction rates) have been shown to be more closely related to the flux of fresh organic carbon to a sediment surface than to the sediment's organic content per se (Kelly and Chynowetu, 1981). Thus, sulfate reduction rates can be substantial given an adequate supply of fresh orgnaic substrate, even though the net accumulation of organic matter, as reflected by the TOC content of a sediment, may be low. Conversely, sulfate reduction rates may be low even in organic-rich sediments, if the primary source of the sedimentary organic material is refractory terrestrial humus.

The availability of reactive iron may be another important factor in controlling the net generation of alkalinity in anoxic lakes and lake sediments. Although iron is the fourth most abundant element in the crust of the earth (Mason and Moore, 1982), reducible iron may not be as abundant in lacustrine systems. For example, in the Lake 223 experiments, hypolimnetic sulfate reduction rates exceeded the rate of supply of reactive iron. This resulted in a net accumulation of dissolved sulfide within the hypoliminion (Cook et al., 1985). In spite of the large reduction rates, however, the net production of alkalinity was limited by the ability of the system to store the sulfur as mineral sulfides. The seasonal alkalinity associated with sulfides in the water column was lost when the sulfides were oxidized at overturn.

Pore water profiles and radiosulfate incubations in softwater lake sediments reveal that sulfate is removed from pore waters at high rates from the upper few to upper 10-15 cm of the sediment column (Rudd et al., 1985; Brunelle, 1985). Pore water profiles in the littoral sediment of lakes in northern Wisconsin (Cook, 1984; Perry et al., 1985) the Adirondack Mountains, New York (Brunelle, 1985; Kelly and Rudd, 1984) southeastern Ontario and southern Norway (Kelly and Rudd, 1984), Florida (Baker, 1984) and northwestern Ontario (Cook et al., 1985) also indicate extensive uptake by sediment microorganisms. Although dissimilatory sulfate reduction in sediments may be widespread in softwater lake systems, it is probable that other biogeochemical processes such as a direct sulfate assimilation and assimilatory sulfate reduction play significant roles in the sedimentary cycling of sulfur.

In Lake 223 at ELA, the amount of sulfur stored in the lake sediments was found to be equal to the amount of sulfate removed from the water column over a three-year period, within the uncertainties of the measurements (Cook and Schindler, 1983; Cook et al., 1985). In another study at the Experimental Lakes Area (ELA), the sedimentary retention of radio-sulfur-labeled iron sulfide and organic matter was found to differ, with iron sulfide oxidized to a greater extent than the organic forms (Rudd et al., 1985). Organic sulfur may be more refractory than the inorganic forms (Howarth, 1984) and, therefore, may be preferentially retained over mineral sulfides. For example, for lakes in the Adirondacks Mountains, New York, organic forms of sulfur account for more than 70% of the sulfur in the sediment (Mitchell et al., 1981, 1984; Brunelle, 1985).

In contrast to opens water systems, reactive iron is not generally a limiting factor for the net production of alkalinity in sediments. Rather, given sufficient metabolizable organic material, sulfate reduction rates tend to be proportional to dissolved sulfate concentrations. For example, in the Lake 223 experiment, sulfate reduction rates increased approximately in proportion to increases in sulfate concentration (Cook and Schindler, 1983). Similarly, sulfate concentration gradients in littoral sediments from a variety of lakes have been observed to be directly related to the sulfate concentration in the overlying water (Kelly and Rudd, 1984; Rudd et al., 1985). Although the details of the sulfate consuming reactions within lacustrine sediments probably vary in different environments (Cook/Holdren/Mitchell, pers. commun.), the potential for sediments to generate alkalinity through any of a number of biogeochemical reactions appears to be proportional to lake water sulfate concentration.

3.7.4.2 Sulfur Cycling in Aquatic Ecosystems

In order to evaluate the whole-lake production of alkalinity from assimilatory and dissimilatory sulfate reduction, a detailed examination of whole-lake sulfur cycles must be done. Few studies of this type have been reported.

Lake 223 at the Experimental Lakes Area has been acidified by experimental sulfuric acid additions rather than from atmospheric deposition. The mass of sulfate reduced in the littoral and profundal sediments was 40% of the total sulfur inputs over an eight-year period (Cook et al., 1985). Of this whole-lake reduction, 70% occurred in littoral sediments and 30% occurred in the hypolimnion. In nearby Lake 114, a lake without a hypolimnion, sulfate reduction in epilimnetic sediments accounted for all of the sulfate loss, which amounted to 36% of the total inputs (Schindler and Turner, 1982).

Alkalinity production from sulfur cycling has also been estimated as the difference between measured inputs, outputs, and change in storage for whole-lakes. It is difficult to assess the importance of alkalinity derived from sulfate reduction as determined from lake mass balances. One problem is that the exact end product of sulfate reduction is typically not determined in such studies. Another is that inputs and outputs of sulfate are typically large in comparison to the quantity of sulfate consumed. For example, in Langtjern (Norway), the calculated percentage of sulfate retained was very small compared to sulfate input (approximately 5%) but this retention could have accounted for about 50% of the alkalinity produced in the lake (Wright, 1983).

An additional problem with lake mass balance studies is that inputs of sulfur from dry deposition cannot be determined with sufficient accuracy (Dillon, 1984). In lakes of the Sudbury area, Jeffries et al. (1984) calculated that unmeasurable SO_2 deposition was 1.2 to 2.6 times higher than the sum of other sources of acidity. For three Adirondack lake watersheds, Galloway et al.

(1983) calculated that the inputs of sulfate equaled or were less than outputs and concluded that sulfate reduction was not important. Such conclusions, however, must be evaluated with an appreciation of the difficulty of obtaining accurate measurements sulfate inputs from dry deposition and outputs in terrestrial runoff. At Woods Lake, one of three lakes studied by Galloway et al. (1983), Rudd et al. (1985) found high rates of sulfate reduction and large quantities of reduced sulfur in the sediments, indicating that some alkalinity may be generated by these processes. In another of the lakes (Sagamore), however, both sulfate profiles in pore water and radiosulfate reduction measurements indicated very little sulfate reduction (Kelly, personal communication).

A detailed, three-year budget of alkalinity, cations, and anions for Lake 239 (Experimental Lakes Area), a small, poorly-buffered lake that serves as a control, revealed that sulfate retention was 20% of the total inputs and accounted for 24% of the in-lake alkalinity production (Schindler et al., 1985). Studies of alkalinity production using water column enclosures (limnocorrals) have also demonstrated the importance of bacterial sulfate reduction in neutralizing acidity in northwestern Ontario (Schiff and Anderson, 1985), northern Wisconsin (Perry et al., 1985), and Florida (Baker, 1984).

3.7.4.3 Nitrogen Transformations and Cycling in Aquatic Systems

Many watershed studies, have shown that inorganic nitrogen is strongly retained by forests in areas susceptible to acidification. When the biological demand for nitrogen in forest ecosystems is exceeded by the available supply from atmospheric deposition and internal sources, increasing amounts of nitrogen will be released to aquatic systems. Also, when lakes are precipitation dominated (i.e., receive a majority of total water inputs from precipitation), nitrogen inputs may be significant.

The biogeochemistry of nitrogen in aquatic systems and its role in surface water acidification are complex and poorly understood. Nitrate uptake by aquatic plants and heterotrophic microorganisms (assimilatory nitrate reduction) as well as denitrification (dissimilatory nitrate reduction) consume one equivalent of hydrogen ion for every equivalent of nitrate reduced (Stumm and Morgan, 1981). Metabolic reactions of ammonium, such as photosynthetic uptake and nitrification, are acidifying processes. The cycling and transformations of nitrogen would therefore be expected to alter the acid-base balance of lakes.

Whether the net uptake of nitrate by aquatic plants represents a permanent source of alkalinity depends on the fate of the organic nitrogen. If the organic nitrogen is decomposed, released, and nitrified within the lake, no permanent increase in alkalinity will occur from the nitrate uptake. Denitrification of nitrate produces N_2O or N_2, which when exchanged with the atmosphere, results in a net gain of alkalinity.

Ammonium reactions need to be considered along with nitrate reactions. Ammonium is typically the second most abundant cation in precipitation and is a dominant component of sulfate aerosols. Ammonium is used by aquatic plants preferentially over nitrate in nitrogen-poor systems (Axler et al., 1982). Ammonium uptake equal to nitrate uptake will result in no net change in alkalinity.

Eutrophication experiments at ELA, in which neutral salts of ammonium or nitrate were added to several lakes, provide a basis for examining the role of nitrogen compounds on the acid-base balance of lakes. Additions of ammonium chloride plus phosphorus to Lake 304 resulted in photosynthetic uptake of these nutrients and an acidification of the epilimnion from pH 6.5 to less than pH 5

(Schindler, 1984; Schindler and Turner, 1985). This acidity was reconsumed during winter when decomposition of organic matter regenerated ammonium.

Ammonium added to this same lake without phosphorus remained in the water column, presumably because the algae were phosphorus-limited. The ammonium concentration increased until nitrification occurred, with a decrease in pH to 4.6 (Schindler and Turner, 1985).

When the fertilization of Lake 304 was changed to nitrate plus phosphorus, alkalinity increased as a result of photosynthetic nitrate uptake (Schindler and Turner, 1985). The efficiency of alkalinity generation by nitrate addition in this experiment was much higher than consumption of alkalinity by ammonium addition, presumably because some of the ammonium taken up biologically was recycled as ammonium during decomposition (Schindler and Turner, 1985).

Permanent sedimentation of nitrogen added as nitrate to ELA Lake 227 averaged 60 to 70% and generated an equivalent amount of alkalinity (Schindler, 1984). Nitrogen not permanently sedimented is released as ammonium upon decomposition and would lead to an acidification when the ammonium is nitrified or taken up by aquatic plants.

Addition of nitric acid alone to ELA Lake 302 (North Basin) has stimulated denitrification greatly and algal uptake slightly (Schindler, 1984). The alkalinity produced by these reactions was nearly 100% efficient in consuming the added hydrogen ion, suggesting that nitric acid may be a less important acidifying agent than sulfuric acid when added during periods of biological activity (Schindler, 1985; Schiff and Anderson, 1985). Episodic additions of nitrate to aquatic systems still present considerable problems, however.

3.7.5 Alkalinity Production by In-Lake Processes

Measurements of in-lake processes resulting in the net production of alkalinity have been made in very few systems (Cook et al., 1984). Estimates of alkalinity production have been made from modeling exercises and from alkalinity input-output budgets. For example, the Trickle-Down Model for Vandercook Lake (a precipitation dominated seepage lake in Wisconsin) predicted that 75% of the alkalinity produced by the entire watershed-lake system was generated in the lake (Schnoor, personal communication). The alkalinity budget for Lake 223 under natural conditions before the acidification experiment began revealed that 85% of the alkalinity in the lake was produced in situ, whereas only 15% originated in the terrestrial watershed (Cook et al., 1985). At two other precipitation dominated seepage lakes in northwestern Wisconsin, about 50% of the lake alkalinity was generated in situ. The processes producing the alkalinity were not measured for these lakes.

In a detailed examination of the alkalinity budget for Lake 223 for the eight-year period after acidification began, Cook et al. (1985) found that 70% of the acid added was neutralized by in-lake processes. The major H^+ consuming process was bacterial sulfate reduction and FeS formation (74% of the total consumption) with littoral sulfate reduction accounting for 52% and hypolimnetic sulfate reduction 22% of the total. Whereas nitrate reduction was a significant generator of alkalinity for Lake 223, its magnitude was very similar to ammonium oxidation, so that the net effect of input-output budgets of inorganic nitrogen was almost zero. The net production of cations in the lake, primarily calcium and manganese, was nearly balanced by the net retention of magnesium, potassium, and iron with the result that 8% of the total consumption of H^+ was by exchange with basic cations.

The rate of alkalinity production in Lake 223 increased four-fold as a result of the acid additions (Cook et al., 1985). Although the exact cause of the increase is not known, bacterial sulfate reduction also increased in response to the acid additions, primarily due to an increase in sulfate concentration. Apparently, the efficiency of the acid additions in acidifying the lake was limited by internal alkalinity generation, which increased as the acidification proceeded.

Long-term input-output budgets for Lake 239, a small poorly-buffered lake at ELA, revealed that 90% of the alkalinity in the lake was generated in situ rather than by reactions with the terrestrial watershed (Schindler et al., 1985). The processes responsible for the generated alkalinity were: (1) exchange of H^+ for Ca^{2+} (55% of the in-lake alkalinity production); (2) retention of sulfate, presumably as FeS (24%); and (3) biological uptake and sedimentation of nitrate (18%).

Seven-year input-output budgets for major ions at Langtjern (Norway) indicated that 70% of the alkalinity in the lake was produced by in-lake processes and 30% was contributed by the terrestrial catchment (Wright, 1983). Bacterial sulfate reduction accounted for 48%, calcium production 37%, and nitrate uptake 15% of the in situ production in Langtjern. For the sulfur budget, a retention of a small amount of the input sulfate (5%) accounts for the majority of the alkalinity production.

Few detailed whole-lake alkalinity budgets have been determined in the eastern United States. On a two-year study of the alkalinity budget of a water supply reservoir in central Massachusetts, Eshleman (1985) found that the reservoir had no large internal sources of alkalinity, although both groundwater seepage and dry sulfur deposition provided alkalinity and mineral acidity, respectively. Ammonium and nitrate budgets indicated algal uptake of equivalent

Table A.3.3. Rates of in-lake alkalinity production.

Site	Rate (meq m^{-2} yr^{-1})	Method	Reference
L223, Pre	88	Whole-lake	Cook *et al.*, 1985
Post	350	Whole-lake	
L239	157	Whole-lake	Schindler *et al.*, 1985
Langtjern	118	Whole-lake	Wright, 1983
Bickford	0	Whole-lake	Eshleman, 1985
Little Rock	140	Flux Method	Cook *et al.*, 1984

quantities and, therefore, no net alkalinity was generated. The reservoir was able to be modeled as an ideal batch reactor for alkalinity.

Rates of in-lake alkalinity production (88-330 meq m^{-2} yr^{-2}; Table A.3.3) are greater than the annual wetfall of acidity for the northeastern U.S. Precipitation of pH 4.2 falling at an annual rate of 1 m represents 63 meq of H^+ m^{-2} yr^{-1}. Because a lake typically occupies 5-20% of the watershed, about 5-20% of the acidity falling on a drainage watershed may be neutralized by in-lake processes. For a precipitation-dominated seepage lake, the in-lake alkalinity production would have the potential to neutralize all of the incident precipitation.

3.7.6 In-Lake Production Relative to Watershed Alkalinity Production

Major ion and alkalinity budgets of watersheds are useful in quantifying the current response of surface waters to acidic deposition. Because of the wide variety of data that have been reported for watershed budgets, it is difficult to calculate precise rates of annual alkalinity production. Furthermore these budgets are complicated by unknown (or unmeasured) rates of dry deposition, mineral sulfide weathering, organic acid production, and ion uptake by vegetation, so comparisons of watershed alkalinity production rates are not trivial.

Nonetheless, using a wide variety of data from the literature, estimates of annual watershed alkalinity production have been calculated (Table A.3.4). The results indicate that annual rates of watershed alkalinity production for a group of softwater systems are in the range 50-500 meq m^{-2} yr^{-1}, with an arithmetic mean of 164 meq m^{-2} yr^{-1}. It should be recognized that many of the values have been corrected for dry sulfur deposition, if reasonable estimates (either from direct measurement, throughfall enrichment, and/or input/output

SO_4^{-2} budgets) were available. Estimates were made for dry deposition at Hubbard Brook, Birkenes, the Adirondacks, Bickford watershed, White Oak Run, and Deep Run. None of the production estimates include a correction for ion accretion in biomass; therefore, the values in Table A.3.4 are conservative estimates.

Comparison of results for in-lake alkalinity generation (Table A.3.3) with rates of watershed alkalinity production (Table A.3.4) reveals that the rates are of the same order of magnitude on a per area basis. Precipitation dominated seepage lakes with low watershed area:lake area ratios (< 2), therefore, could potentially be dominated by in-lake alkalinity production. This appears to be the case for some lake-watershed systems in the Upper Midwest of the U.S. (Gherini, personal communication; Schnoor, personal communication). Canada (Schindler et al., 1980). Based on a survey of 147 lakes, the estimated mean watershed area: lake area ratio for the lakes in the DDRP target population was about 19. The DDRP target population includes an estimated 4227 lakes in the northeast. For the majority of these lakes, in-lake alkalinity generation probably would be at least an order of magnitude less than watershed alkalinity production.

3.7.7 Expected Range and Regional Distribution

Data do not presently exist from which to estimate either the expected range or the regional distribution of net alkalinity production values within aquatic systems by any one process or by all processes combined. Several generalizations, however, do seem reasonable. The in-lake alkalinity production processes are likely to be related to: (1) hydraulic retention time; (2) ratio of lake volume to sediment (or lake surface) area; (3) nutrient status; (4) hydrologic type.

Table A.3.4 Annual net watershed alkalinity production (meq m^{-2} yr^{-1}) of softwater systems.

Watershed	Annual Alkalinity Production	References
(1) Hubbard Brook, NH	123	Likens *et al*, 1977. Driscoll and Likens, 1982.
(2) Birkenes, Norway	91	Wright and Johannessen, 1980.
(3) Adirondacks, NY		
(a) Woods Lake	101	Goldstein *et al*., 1984.
(b) Panther Lake	216	Goldstein *et al*., 1984.
(4) Bickford Watershed, MA	109	Eshleman (1985)
(5) Findlay Lake, WS	481	Richey and Wissmar, 1979. Wissmar *et al*., 1982. Powers and Rambo, 1981. Duncan and Aussever, 1984.
(6) H. J. Andrews, WS#10, OR	144	Sollins *et al*., 1980.
(7) Bowl Watershed, NH		Martin, 1979.
(a) Subwatershed E	195	Martin, 1979.
(b) Subwatershed W	236	Martin, 1979.
(8) Coweeta (#18), NC	183	Swank and Douglas, 1977.
(9) White Oak Run, VA	120	Shaffer (pers. comm., 1985).
(10) Deep Run, VA	111	Shaffer (pers. comm., 1985).
(11) Lower Mersey River, Nova Scotia	54	Kerekes, 1980.
(12) Harp Lake, Ontario	130	Dillon *et al*., 1982.

Lakes with short water residence times will not have the degree of interaction with bottom sediments as lakes with longer residence times, and therefore, will not have as large an in-lake alkalinity production. For example, in-lake alkalinity generating reactions are occurring at considerable rates in the sediments ot the Big Moose Lake system (Kelly and Rudd, unpublished data). The residence times for this system, however, is a few months, and the flux of alkalinity from the sediments into the water column does not occur at a fast enough rate to affect the limnetic alkalinity significantly.

Lakes with shallow mean depths (lake volume divided by sediment area) will have more interactions between sediment-derived ions and the water column than lakes with deeper mean depths.

The nutrient status of a lake may also influence the alkalinity produced by anabolic and catabolic processes. An abundant nutrient supply would promote high deposition of organic matter, which in turn would provide the organic substrate for dissimilatory nitrate and sulfate reduction. A high supply of nutrients would also promote assimilatory sulfate and nitrate reduction. A nutrient-impoverished lake may not be able to maintain high levels of microbial activity and, thus, may not be able to generate significant amounts of alkalinity by metabolic processes.

The export of acidity from terrestrial watersheds is a function of the hydrologic flow path, with shallow flow promoting higher acid loading than deeper flow. Lakes having catchments with thin overburden will have proportionally more opportunity for acid neutralization in the lake than lakes having catchments with thick overburden. Those lakes receiving most of their input water from precipitation (i.e., precipitation-dominated seepage lakes) will have the maximum opportunity to modify the alkalinity by in-lake processes. Thus, precipitation-dominated lakes and lakes having catchments with thin overburden will be the most sensitive to the generation of alkalinity by in-lake processes. For typical lake-watershed systems in the northeastern U.S. with watershed area:lake area ratios in the range 10-20 watershed biogeochemical processes will typically provide virtually all of the alkalinity produced by the system.

3.7.8 Threshold Values for In-Stream and In-Lake Alkalinity Production for Direct/Delayed/Capacity Protected Systems

Based on the limited data presently available, it is not possible to specify the threshold values of net annual alkalinity production that might tend to be correlated with direct-response, delayed-response, and capacity-protected systems. Furthermore, it seems most unlikely that such specific thresholds exist, since the response of a watershed system reflects the net or integral response of numerous biogeochemical processes occurring along several alternative flowpaths, only one of which is net alkalinity production processes within aquatic systems.

Given that lake sediment and water chemistry are to a large extent the product of the geology, hydrology, and soils in the surrounding watershed, there may be a reasonable correlation between values of net annual alkalinity production in streams and lakes and indices of the relative importance of alternative hydrologic pathways and biogeochemical processes in the terrestrial system.

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Chapter 4

A Review of Methods for Assessing Aquatic System Response

by

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4.0 A REVIEW OF METHODS FOR ASSESSING AQUATIC SYSTEM RESPONSE

4.1 INTRODUCTION

As described in Chapters II and III of this document, there are a number of watershed processes and characteristics that may critically influence the response of aquatic systems to acidic deposition. The relative importance of each of these factors may vary considerably among systems, thus making the problem of determining the response characteristics of all surface waters in a region a complex one. In light of this complexity, it is worth reviewing the methods that can be used to assess the response characteristics of aquatic systems.

A variety of methods can be used to gain insight into the response characteristics of an individual system or the distribution of characteristics of a number of systems. These methods range from classification based on historical trends in chemistry or current chemical conditions to detailed analyses of complex dynamic models that integrate a number of watershed processes. In this chapter, we will review each of these methods, emphasizing their potential utility in classifying systems with regard to their response characteristics to acidic deposition. We begin with an overview of the methods, divided into five general classes. Each of these methodological classes is discussed in detail following this overview.

4.1.1 Historical Trends Analysis

This method involves analyzing historical information on changes in lake chemistry to determine how systems have responded (if at all) to inputs of acidic deposition. Such an analysis obviously requires scientifically defensible data on trends in both lake chemistry and deposition. Although historical measurements of lake chemistry are available for many systems, the quality of much historical data is questionable (Church, 1984). Analysis of lake sediment cores, particularly for the species composition of acid-sensitive species such as diatoms, has also been used, together with core dating methods such as ^{210}Pb analysis, to infer historical trends in lake chemistry (Norton, 1984). Inasmuch as historical deposition data are virtually nonexistent, deposition typically is inferred from historical emissions data.

In general, these methods are useful for approximate evaluations of how systems have responded to acidic deposition in the past. Their use for classifying future response of systems, however, may be rather limited, as discussed below in Section 4.2, Historical Trends Analysis.

4.1.2 System Descriptions

System description is the title given to a general category of methods, all of which involve consideration of the current status of an aquatic system or its surrounding watershed. To use any of these methods to assess system response, one needs to hypothesize the relationship between the current status of a system and its expected response characteristics. For instance, one might postulate that surface water alkalinity is a reasonably good indicator of the characteristics of the response of a system to acidic deposition. For these approaches to be considered valid, the hypotheses inherent within them need to be supported by other analyses, such as those described in later sections.

Analyses that fall into the category of system descriptions include:

o analyses of the frequency distributions of surface water chemistry characteristics (such as alkalinity) across a number of aquatic systems;

- multivariate analyses of the relationship between watershed characteristics thought to influence system response and surface water chemical conditions; and
- statistical analyses of the relationships between surface water chemistry and inputs of acidic deposition.

4.1.3 Steady State Models

A number of models exist of aquatic system response to acidic deposition. These models can be used to predict the eventual chemical state that will result from a given level of deposition. The models range from very simple empirical models, to steady state solutions for more complex, dynamic models.

Inasmuch as steady state models have no time component, they cannot directly be used to discriminate among natural systems with regard to their dynamic response characteristics. They can be used, however, to make this distinction indirectly (see Section 4.4, Steady State Models). A significant advantage of these simple models, as compared to the more complex models, is that they can be applied directly to large numbers of systems.

4.1.4 Single Factor Response Time Estimates

Four factors that appear to play a central role in determining the response characteristics of an aquatic system are hydrologic flow path, weathering replacement, base cation supply and sulfate adsorption of its associated catchment. It is possible using simple formulations for these processes to estimate potential soil contact time, or for a given atmospheric input, mineral weathering rates or the time to reduce the base saturation or exhaust the capacity of a particular soil to adsorb sulfate. Such estimates require laboratory measurements of soil chemical characteristics plus estimates of sulfur inputs to the system. These order of magnitude estimates of response time can be used to rank response times of lake/watershed systems.

4.1.5 Dynamic System Models

The final class of methods for characterizing response characteristics of aquatic systems to acidic deposition is that of dynamic system models. Such models can be used to attempt to integrate the many processes that influence system response to acidic deposition into a framework that allows one to predict how that system (or systems) will change over time. These models are both dynamic and integrated. Therefore, they are potentially much more useful than are the previous two methods for directly classifying systems according to their response times. On the other hand, their complexity and sometimes relatively extensive data requirements makes their application to a large number of aquatic systems virtually impossible. Their greatest utility lies in providing an integrated framework for identifying those factors most important, individually or in combination, in determining response characteristics of systems. Once these factors have been identified, it is not necessary to apply the models directly to all (or even many) systems to obtain classification. Rather, one simply has to characterize each system as to the combination of those factors that are present, and from this determine their response characteristics.

There are a number of models of this type that are generally recognized as reasonable representations of aquatic systems and their watersheds, at least for certain geographical areas. Given the potential utility of these models as classification tools, and given their inherent complexity, considerable attention will be devoted to each of these models in the sections that follow.

4.1.6 Integration

The value of any one approach to classification is greatly reduced when considered in isolation rather than alongside several other approaches. There is still a great deal of uncertainty associated with our understanding of the processes that influence surface water acidification. Thus, the credibility of any classification based on a single approach is greatly enhanced if other, independent approaches result in a similar classification. Conversely, when different approaches result in contrasting classifications, we are made more aware of the limitations of these approaches, and sometimes even the source of those limitations (i.e., which processes are missing from the analysis). Therefore, it is important to consider the merits of each approach in the context of the others. Specifically, the question should be asked, "How can this approach complement or supplement other approaches to classification?"

4.2 HISTORICAL TRENDS ANALYSIS

4.2.1 Approaches

The basic idea of historical trends analyses is to relate some measure of historical patterns of deposition to some other measure of changes in surface water chemistry. With this information, one can evaluate whether a particular aquatic system appears to have responded to changes in acidic deposition and, ideally, the rate at which the system responded. If such information can be obtained for several systems, it may be possible to identify differences among these systems that are related to their response characteristics (e.g., depth of permeable material, predominant soil types present). This type of knowledge might then be applied to other areas, where acidic deposition has only more recently increased, to assess the expected future response of surface waters in those areas.

There are virtually no historical records of acidic deposition rates for time periods prior to 1970. On the other hand, historical records of SO_x emissions are available (e.g., OTA, 1984), and have been used as surrogate measures of changes in acidic deposition. Although a direct relationship between emissions for a specific region and deposition in that region almost certainly does not exist, the two are likely to be correlated with each other.

Historical data on lake chemistry, particularly pH and alkalinity, are available for many systems, but severe methodological problems cast doubt on the interpretation of much of this data (for a discussion of this issue, see Church, 1984; Kramer and Tessier, 1982; 1983). These problems are often compounded by the lack of detailed documentation of the methods used in the earlier studies.

Indirect information on changes in lake chemistry can also be obtained from analyses of core samples taken from sediments. These sediment cores often provide a detailed record of changes in physical, chemical, and biological features of the lakes that have occurred over a considerable period of time. Isotopic dating techniques such as ^{210}Pb analysis can be used to "time-calibrate" the core and thus aid interpretation. The most commonly used indicator of historical chemical changes associated with acidification are diatoms. Diatoms appear to be relatively sensitive indicators of pH, with different species being sensitive to different pH levels. Thus changes in diatom species composition through a sediment core can be used to infer changes in lake pH. Other indicators of change in lake pH have also been considered, including the apparent deposition rate of pH sensitive metal species such as Zn and Mn.

4.2.2 Previous Applications

Numerous analyses of historical surface water chemistry data have been conducted (e.g., Beamish and Harvey, 1972; Beamish et al., 1975; Davis et al., 1973; Haines and Akielaszek, 1983; Norton et al., 1981; Pfeiffer and Festa, 1980; Schofield 1976a, b; Smith and Alexander, 1983; Watt et al., 1979), and many of these have documented significant changes through time. More recently, Hendrey et al. (1984) have compiled an extensive data base (the Acidification Chemistry Information Database -- ACID) of time series of surface water chemistry throughout the U.S. Their analyses indicate recent temporal trends in surface water chemistry (sulfate, alkalnity, pH) that are consistent with trends in recent emissions of acid precursors. For instance, sulfate concentrations are declining in the northeastern U.S. and increasing in the Southeast; emissions trends in these two regions also indicate recent decline and increases, respectively. A strength of this study was the large number of stations, the data used and the emphasis on regional analyses. Significant drawbacks, however, were: (1) the inclusion of data from stations in very large and heavily developed watersheds; (2) the absence of complete quality assurance/quality control of the data used; and (3) the variations in numbers and locations of stations used over the period of time examined in the study.

Analyses of trends by paleolimnological methods (i.e., sediment core analysis) have also been carried out by a number of researchers (Davis et al., 1983; review by Batterbee, 1984). As with the historical chemistry analyses, clear patterns have been detected that are most likely indicative of changes in surface water chemistry. These methods are not very precise, however, and are thus generally not useful for a detailed analysis of the time scale of these changes.

4.2.3 Advantage and Disadvantages

The obvious advantage of historical trends analyses is that they are the only possible means by which we can document that: (1) changes have occurred; and (2) that these changes are associated with changes in atmospheric levels of sulfur. Thus, these methods play a vital role in demonstrating that some aquatic systems do (or will) respond to changes in acidic deposition.

Most of the disadvantages of these approaches are methodological, and have already been referenced. Historical chemistry data are often suspect and the interpretation of sediment cores remains as much an art as a science. As a method of classifying systems according to their anticipated future response characteristics, these approaches have other disadvantages. Very little, if any, of the information from historical trends studies can be used to evaluate the rate of response of systems when subjected to a certain deposition rate.

4.2.4 Expected Utility

The principal utility of historical trends analyses has been to document that changes in surface chemistry have occurred in the past and that these changes appear to be related to changes in deposition rates. This information could be used to help delimit those systems that have already responded to acidic deposition (but see 4.3). The methodological problems associated with these approaches, however, severely limit their utility as means of determining the expected dynamic response characteristics of systems that have not already responded.

4.3 SYSTEM DESCRIPTIONS

4.3.1 Approaches

The common element of each of the three approaches that fall into this category is that they are all based on the direct interpretation of current surface water chemistry. Other approaches (Section 4.5 Single Factor Response and 4.6 Dynamic Models) use information on current conditions, but explicitly attempt to predict future chemical changes.

The first approach involves a simple assessment of current chemical conditions in a number (preferably large) of systems. To some extent, the present level of chemical variables such as alkalinity or base cations are an indication of the likely response of a system to current levels of deposition. For instance, lakes with alkalinities greater than 400 ueq/l are unlikely to become acidic under current deposition levels anywhere in the U.S. In fact, this alkalinity threshold may actually be much lower, but 400 ueq/l provides a conservative estimate.

Given such an assumption/hypothesis about the range of a chemical variable that is associated with or indicative of a particular type of response, frequency distributions of that variable across a set of surface waters -- preferably a representatively sampled set such as the NSWS lakes -- can be used to estimate the proportion of surface waters in a region that exhibit certain response characteristics.

The second approach considers the relationship between current chemical conditions (especially pH and alkalinity) and various watershed characteristics hypothesized to influence water chemistry. Generally this type of analysis is accomplished using multivariate methods (e.g., multiple regression or discriminant analysis).

This type of statistical analysis does not directly provide an alternate method of classifying systems, but rather, provides empirical support for the time-varying analyses described later (Sections 4.5, Single Factor Response Time Estimates and 4.6 Dynamic Models). If certain watershed characteristics (e.g., depth of permeable material) significantly influence current alkalinity, then one would expect such factors to be very important in the dynamic models.

The third approach is designed to assess whether a watershed is retaining sulfate. This is accomplished by computing a simple input-output budget for sulfate for any watershed where surface water sulfate concentration measurements are available. Total sulfur deposition is calculated from wet deposition data and estimates of dry deposition, and corrected for evapotranspiration to give a measure of input concentrations. This value is compared to current sulfate concentrations in surface waters. If surface water concentrations are less than input concentrations, then the watershed appears to be retaining sulfate. If the two are equal, then no net retention is occurring.

Extent of sulfate retention is an indication of how a system may eventually respond to acidic deposition. The results of this analysis can be compared to the time varying analyses to test for consistency among analytical approaches.

4.3.2 Previous Applications

The characterization of the geographical distribution of potentially sensitive or acidified waters has received considerable attention in the U.S. (Hendrey et al., 1980; Haines and Akielaszek, 1983; Omernik and Powers, 1982) and elsewhere (Kelso et al., in preparation; Wright and Snekvik, 1978; Almer et al., 1978). Omernik and Powers (1982) have attempted to summarize information on surface water alkalinity in the U.S. into maps that describe the regional distribution of waters with differing alkalinity ranges. These maps are extremely useful as descriptions of the broad extent and location of potentially acid sensitive waters. They were not designed (i.e., mapped to a scale) to indicate fine-scale heterogeneity in surface water alkalinity.

One of the problems with most of these studies is that the information was not obtained from a statistically representative sample of the surface waters in an area. The National Surface Water Survey was designed explicitly to overcome this difficulty by selecting lakes and streams from potentially sensitive areas using a stratified random sampling procedure. Thus, these data can be used to provide an unbiased estimate of the number of lakes or streams in a region that fall into different categories of chemical status (e.g., alkalinity classes).

Generally, these synoptic analyses of water chemistry have not been used to classify systems according to their response characteristics. Synoptic data could be used for this purpose, however, given an assumption about how current status is related to expected (or already observed) response to acidic deposition.

Some of the aforementioned studies of the regional distribution of surface water characteristics also attempted to relate surface water chemistry to soil and bedrock characteristics (e.g., Hendrey _et al_., 1980; Haines and Akielazsek, 1983) and found good correlations. These analyses were generally carried out over widely ranging conditions (i.e., both highly "sensitive" or acidic systems and very "insensitive" systems were included) and thus these correlations are hardly surprising. More recently, Nair (1984) attempted a more detailed regression analysis of factors that were hypothesized to influence lake alkalinity for 229 lakes in the Adirondacks. Again, good correlation was found and a regression equation to predict alkalinity was developed ($r^2 = 0.58$). This equation included soil cation exchange capacity, lake elevation, and a qualitative bedrock sensitivity index. When lakes with alkalinity in the range of only 0-200 ueq/l are considered, however, the accuracy of the regression equation does not appear to be nearly as high. Presumably, more detailed information on soils and other watershed characteristics (e.g., depth of permeable material) could greatly improve the predictive power of multiple regressions such as this.

Thompson and Hutton (1982) compared sulfate wet deposition to surface water sulfate levels at a number of locations across eastern Canada and found concentrations in surface waters to be higher than expected based on wet deposition alone (corrected for evapotranspiration). They attributed this deficit to dry deposition of sulfate, rather than sources in the watershed. More recently, Marmorek et al. (in preparation) attempted a crude input-output budget, also for lakes in eastern Canada, and observed much lower lake sulfate concentrations in regions of northeastern Ontario than would be expected from wet deposition estimates, corrected for evapotranspiration. This result may be indicative of significant sulfate retention in these areas, although the soils typically found in these areas are not generally associated with high sulfate adsorption capacities.

4.3.3 Advantages and Disadvantages

The principal advantages of all of these approaches is that they are easily applied to large data sets, thus allowing a direct examination of the regional distribution of response characteristics. They also require only current information, so the methodological problems associated with interpreting historical data are avoided. The third approach, sulfate input-output analyses, is perhaps the most promising, because it focuses on a process that may be closely associated with the response characteristics of systems.

The major disadvantage of all these approaches (especially the first two) is that they rely on assumptions regarding how a static feature of a system is related to its dynamic response characteristics. Given that these assumptions can be verified by other analyses, these methods provide relatively easy and extensive (data rich) tools for regional characterizations. Without such verification, these approaches can only be considered speculative.

4.3.4 Expected Utility

From the preceding discussion, it is evident that the utility of these methods would be strengthened by support from other analyses. Given that the dynamic approaches described in Sections 4.5 and 4.6 provide insights into the characteristics of lakes and watersheds that influence response times to acidic deposition, these methods will be very useful in aiding the regionalization of the results obtained from a small set of intensely studied systems.

4.4 STEADY STATE MODELS

4.4.1 General Approach

Steady state models of acidification are designed to predict the eventual surface water chemistry that will result from a given level of acidic deposition. The models are typically quite simple, involving only small numbers (< 10) of inputs and outputs. The multitude of interactions that play a role in the acidification/neutralization process are usually aggregated into a few "lumped" parameters that are presumed to represent adequately the complexity of the system. Because they are all simple and have relatively minor data requirements, they can often be applied on a regional basis and thus directly provide extensive predictions of eventual effects.

An important aspect of these models from the point of view of assessing system response is that they all, by definition, lack a temporal element. Thus, they cannot be used to evaluate the rate of response of systems to acidic deposition. Some of these models have dynamic versions that may be used for the rate question. Others have been developed directly from empirical observations or simple theoretical concepts, without any consideration of a time scale. Members of the latter group are somewhat less complex. They will be discussed first.

4.4.2 Examples of Steady State Models

Almer *et al*. (1978) and Henriksen (1980) developed simple, empirical models that graphically relate a measure of acidic inputs (lake sulfate concentrations) and a measure of lake sensitivity (unspecified in Almer *et al*.; calcium plus magnesium in Henriksen) to the expected eventual pH of a particular system. The models were developed to explain patterns of surface water chemistry in lakes in Scandinavia, but more recently attempts have been made to apply them to North American lakes (e.g., Haines and Akielaszek, 1983).

These models have a number of problems that limit their use as tools for predicting effects of acidic deposition. First, the absence of an objective means of classifying lake sensitivity in the Almer *et al*. model makes it virtually impossible to use this model as a predictive tool. Second, both models have assumed that the lakes used in developing them are in steady state with current deposition levels. Third, the presumed relationship between lake sulfate concentrations and sulfur loadings is unlikely to be universal. Thus lake sulfate is probably not a good predictor of loadings for regional application. Finally, Henriksen's model initially assumed that base cation leaching does not increase in response to increased incoming acidity. More recently, Henriksen (1982) relaxed this assumption, and Wright (1983) incorporated a "base cation increase factor" into a modified version of the Henriksen model. Nevertheless, a single constant parameter is probably an inadequate representation of the processes it is intended to reflect, especially when considered on a regional basis.

Thompson (1982) developed a steady state model that is quite similar to Henriksen's, although it is derived from theoretical considerations rather than from empirical observations. Thompson's model also predicted surface water pH from sulfate concentrations (used again as a surrogate for loadings) and cation levels. She represents the effects of cations in terms of a cation denudation rate, which effectively determines the ability of a system to neutralize incoming acidity (i.e., each equivalent of cations neutralizes an equivalent of acidity). Predictions of steady-state pH are derived from considerations of charge balance and carbonate-bicarbonate equilibrium chemistry. For the latter, an assumed CO_2 partial pressure is required. As for the previous models, the supply of base cations (= cation denudation rate) is assumed constant, regardless of the level of acidic deposition.

Thompson has applied the model to several systems in eastern Canada, with reasonable success. The model has the same conceptual weaknesses as Henriksen's, however (sulfate loadings estimated indirectly, base supply constant), and these limit its application on a regional basis or for scenarios of changing deposition.

Marmorek _et al_. (in preparation) have developed a steady state model that is a solution to a very simple dynamic mass balance model for alkalnity, base cations, and sulfate. The basic principles of the model are quite similar to those of Henriksen (1982) and Wright (1983), particularly in that they allow base cation supply to be affected by sulfate loadings. Following Wright, they estimate the acid neutralizing capacity of a watershed from current surface water cation and sulfate concentrations, but do not assume these values to be in steady state. Also, sulfate loading is estimated directly from deposition data, rather than from surface water sulfate concentrations. Thus, the three key assumptions of the earlier models have been relaxed. This model has been used to estimate regional impacts of acidification in eastern Canada (Jones *et al.*, in preparation) but has not been adequately verified to date.

Schnoor *et al.* (1982) also have developed a steady state model based on an alkalinity mass balance. The model was developed as a "lumped parameter" steady state version of the dynamic, Trickle-Down model described in a later section (4.6.4, Trickle-Down model). Deposition data are used as inputs, and acid neutralization is represented by a single parameter, which may vary with deposition. Schnoor *et al.* discuss this parameter in terms of watershed base cation supply and weathering rates and emphasize the importance of knowing whether and how these rates are affected by the amount of incoming acidity. The model has been applied to lakes in Wisconsin and the Adirondacks.

Finally, Reuss (1980, 1983) and Reuss and Johnson (1985) have developed an equilibruim soil and surface water chemistry model that is quite different from all of the previous models. It is considerably more detailed than the others, and is not explicitly concerned with addressing the effects of acidic deposition on the eventual state of an aquatic system. Rather, it predicts the expected equilibrium condition of soil and surface waters over a relatively short time period (the time it takes for precipitation inputs to pass through the soil to surface waters). The Reuss model is, however, incorporated into

MAGIC (Cosby et al., 1984, described in Section 4.6.5, MAGIC), a dynamic model developed specifically to address the issue of long term acidification.

The model accounts for the chemical equilibria associated with cation exchange, aluminum dissolution, and inorganic carbon. Its intent is to examine the effects of increases in the concentration of a mobile anion (sulfate) on the alkalinity of soil solutions. Depending on whether alkalinity is positive or negative, the resulting effects on surface water pH can be dramatically different when this soil water becomes isolated from the ion exchange sites of the soil horizons and CO_2 partial pressure decreases due to contact with air. The most important contribution of this model is that it illustrates a mechanism by which surface water acidification can occur as a result of inputs of sulfate without significant decreases in soil base saturation.

Reuss and Johnson (1985) also point out that the rate at which this effect will occur depends on whether the soils have some capacity to adsorb sulfate, and how long it takes this capacity to be exhausted. They do not account for sulfate adsorption in their model (nor do any of the other models discussed above), although this process is incorporated into the MAGIC model.

4.4.3 Advantages and Disadvantages

The principal advantage of all but the last of the models discussed in this section is that their simplicity allows them to be applied on a regional scale, using only water chemistry and deposition data. The price of this simplicity, however, is that assumptions that are not easy to defend must be made regarding the value of critical parameters such as the base cation increase factor used by Wright (1983) and Marmorek et al. (in preparation). Related to this assumption is the potential danger that watershed neutralization processes are not represented in sufficient detail to be realistic.

Finally, because they lack a time component, they cannot be used to estimate the rate of response of systems to inputs of acidic deposition.

4.4.4 Expected Utility

Given the disadvantages discussed in the previous section, the utility of these models as tools for assessing response characteristics of aquatic systems must be considered quite limited. Nevertheless, they are the only models that can realistically be applied directly on an extensive basis, and thus may prove useful as checks on other approaches to regional estimation of system response characteristics (i.e., dynamic models/surveys).

4.5 SINGLE FACTOR RESPONSE TIME ESTIMATES

The capacity of terrestrial systems to neutralize acid deposition inputs is (apparently) influenced by four major processes: hydrologic flow path, weathering replacement, sulfate retention, and ion exchange buffering (NAS, 1984). These four dynamic processes were discussed in Chapter 3, Current Understanding of Key Factors Hypothesized to Control Surface Water Acidification. Analytical approaches for predicting system response times based on these individual dynamic processes are discussed below.

4.5.1 Hydrologic Flow Path

Terrestrial systems neutralize acidic inputs through sufficient soil contact with soil adsorption-exchange processes (e.g., sulfate adsorption and cation exchange). Two factors -- length of the flow path and reactivity of the flow path -- influence the aquatic system response.

4.5.1.1 Approach

Because precipitation and runoff are time-varying, the "length" of the flow path can be expressed in units of time to estimate the aquatic response. For precipitation to flow through deep soils to a stream or lake, it must not be retained, evaporated, or transpired in the upper soil horizons. That is, it must infiltrate to a saturated level in the soil (Chen et al., 1984). Dominant lateral water movement toward the lake begins in the saturated zone. The rate of this water movement can be estimated by Darcy's Law:

$$Q_{LF} = KAS$$

where Q_{LF} is the lateral flow in cubic meters per day, K is the saturated hydraulic conductivity in meters per day, A is the cross sectional area for flow in square meters, and S is the hydraulic gradient in m per m (vertical per horizontal unit (Chen et al., 1984). Maximum Q_{LF} rates occur when the entire depth of permeable material is saturated.

Various approximations permit the use of this equation. For example, hydraulic conductivity estimates for various consolidated and unconsolidated materials may be obtained from Davis (1969). The cross-sectional area, A, can be approximated by multiplying the lake perimeter and average thickness of the permeable material (Chen et al., 1984). The hydraulic gradient may be estimated from the average basin slope. The flow rate, Q_{LF}, can be normalized by watershed area for comparison with precipitation inputs. If the areal flow rate (m/yr) is much greater than the annual precipitation rate (corrected for evapotranspiration), the potential watershed flow capacity may permit flow through deep soils and sufficient soil contact time for neutralization. If the areal flow rate is comparable or less than the annual precipitation rate, the potential watershed flow may be through shallow soils not permitting sufficient contact time to neutralize acidic deposition. The interaction between soil reactivity and flow volume dictate the capacity of the soil to neutralize acidic inputs. The areal flow rate provides one indicator of this potential for neutralization.

4.5.1.2 Previous Applications

A similar approach was used by Chen _et al_. (1984) to assess water chemistry differences between Woods and Panther Lakes. Woods Lake, an acidic system, had a low potential flow capacity (e.g., 19 cm/yr) in comparison to the mean annual precipitation rate (80 cm/yr). This indicated most of the inflow to Woods Lake did not take a deep flow path through the soil. Panther Lake, a non-acidic system, had a high potential flow capacity (e.g., 600-770 cm/yr) compared to the mean annual precipitation rate (80 cm/yr). Panther Lake had a deeper flow path for inflow to the lake. During snowmelt, however, a portion of the inflowing water could take a shallower path and introduce acidic water to the lake surface.

4.5.1.3 Advantages and Disadvantages

Advantages of this approach are:

- Data are generally available to permit the application.
- It can be applied with minimum time and expense
- It estimates the "length" of the flow path or potential soil contact.

Disadvantages of this approach are:

- Numerous approximations are required for watershed parameters.
- It assumes constant conditions for many watershed properties such as soil moisture content and saturation depth.
- It provides only an indirect estimate of soil contact and the depth of flow.

4.5.1.4 Expected Utility

This approach can provide an additional estimate of aquatic system response that can corroborate, or fail to corroborate, other estimates. Results may indicate whether soil processes will have sufficient contact time for neutralization.

4.5.2 Weathering Replacement

Weathering replacement of exchangeable base cations is a function of atmospheric inputs, mineralogy, base selectivity rates and other factors. Cation exchange is discussed in Section 4.5.4, Ion Exchange. These paragraphs will discuss time estimates of mineral weathering replacement of base cations.

4.5.2.1 Approach

Fractional order kinetics are used in the Trickle-Down model to describe mineral weathering rates as a function of hydrogen ion concentration in bulk solution (Section 4.6, Trickle-Down model). This kinetic, and conceptual, approach to mineral weathering can be used to estimate the long term response of aquatic systems to acid deposition.

Mineral dissolution or weathering rates are proportional to a multiple or power of the hydrogen ion concentration. Fractional order kinetics, which can be expressed as:

$$\begin{array}{c}\text{Mineral}\\ \text{Dissolution}\\ \text{Rate}\end{array} = [H^+]^m$$

[where $m < 1.0$ (Stumm _et al._, 1983)] imply that this multiple or power is less than unity.

This general equation states that as acid deposition increases, the hydrogen ion concentration will increase with a proportional increase in mineral weathering rate. Because of fractional order kinetics, however, a doubling of the hydrogen ion will result in less than a doubling of the mineral weathering rate.

The reaction order, m, is a function of many factors including the specific mineral, soil organic content, etc. and varies from about 0.3 to 0.8. Soil mineralogy, deposition, and soil hydrogen ion concentration data permit order of magnitude estimates of the mineral weathering rates. This information can be integrated with ion exchange estimates (Section 4.5.4) to obtain order of magnitude time estimates for base supply rates and, therefore, the response time of various aquatic systems to rates of acidic deposition.

4.5.2.2 Previous Applications

Schnoor and Stumm (1984) used a similar approach in evaluating important processes in the acidification of terrestrial and aquatic systems. Although there are no studies similar to those proposed, dissolution studies have been done by Busenborg and Plummer (1982), Grandstaff (1977), Schott *et al*. (1981), Stumm *et al*. (1983), and others (See Section 4.6, Trickle-Down Model).

4.5.2.3 Advantages and Disadvantages

Advantages of this approach are:

- Order of magnitude time estimates for mineral weathering rates can be obtained at minimum time and expense.
- Relative comparisons can be made of mineral weathering with other soil processes, such as depletion of base saturation.
- These rate estimates can be compared with rate estimates used or computed by dynamic models for corroboration.

Disadvantages of this approach are:

- These studies were conducted under controlled laboratory conditions and may not be relevant to field situation.
- Mineral dissolution rates are influenced by many factors in addition to hydrogen ion concentration.
- There is no distinction between primary and secondary mineral weathering or weathering order.

4.5.2.4 Expected Utility

Estimates of mineral weathering rates can be computed from soil mineralogy, deposition, and soil hydrgen ion concentration. These weathering rate estimates can be compared with deposition rates to assess the potential depletion of the base cations from the watershed.

4.5.3 Sulfate Adsorption

The two major anions introduced to terrestrial systems through acid deposition are sulfate and nitrate. These anions are provided by sulfuric and nitric acid, respectively. The sulfate anion is assumed to be the dominant anion in surface water acidification (NAS, 1984) and its biogeochemical dynamics were discussed in Chapter 3.3, Anion Mobility, Part A. This discussion will focus on estimating aquatic system response time from sulfate adsorption dynamics.

4.5.3.1 Approach

Sulfate adsorption in soils occurs primarily by specific adsorption (OH^- ligand exchange) on iron and aluminum hydrous oxide coatings and soil clays (Kingston _et al_., 1972; Johnson and Todd, 1983; Rajan, 1978). Equilibrium between adsorbed and dissolved sulfate may be described by a Langmuir isotherm or hyperbolic function (Figure A.4.1). Using sulfate adsorption isotherms and estimated sulfate deposition levels, the soil can be "titrated" (theoretically) to describe the time required to reach the steady state condition (i.e., no net SO_4 adsorption on an annual basis). This is shown schematically in Figure A.4.1.

4.5.3.2 Previous Applications

There are no previous applications of this approach but it is similar to the steady state model "titrations" of Henriksen (1890, 1982), Wright (1983), and Schnoor (1983).

4.5.3.3 Advantages and Disadvantages

Advantages of this approach are:

- An estimate can be obtained of the time to reach steady state under present or alternative deposition levels.
- This estimate can be compared with dynamic model predictions and input-output budgets for corroboration.

Disadvantages of this approach include:

- This approach does not consider other chemical or biologically mediated transformations that can increase sulfate retention.
- The sulfate adsorption isotherms must be measured at soil pH because these isotherms are pH dependent.

4.5.3.4 Expected Utility

This approach provides an estimate of the relative importance of this process compared with other soil processes. In addition, time estimates to reach steady state (i.e., no net sulfate adsorption) can be computed for

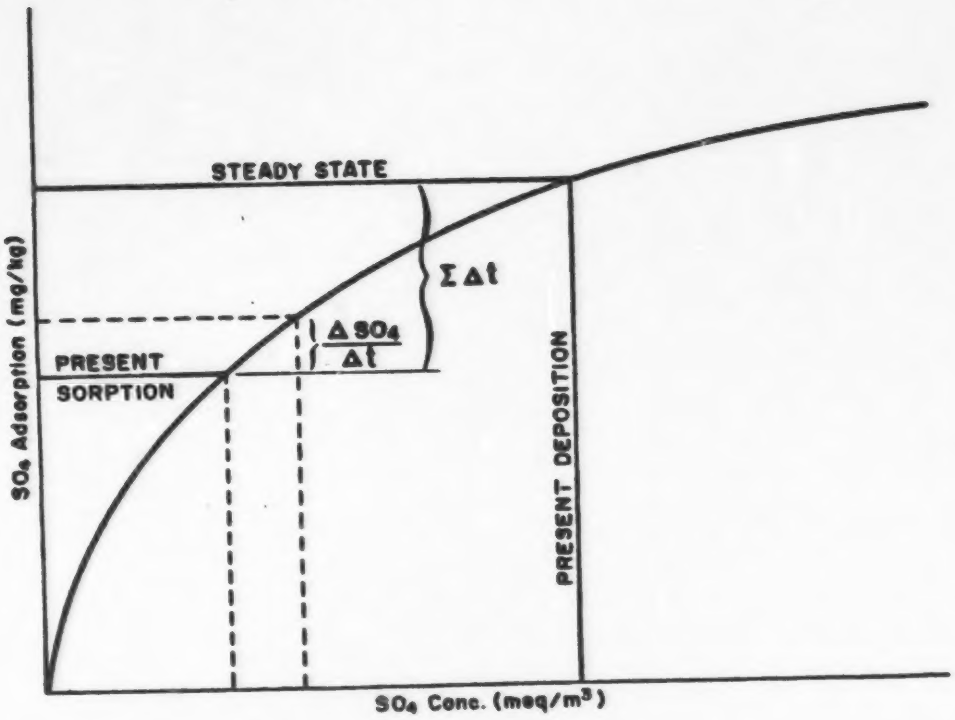

Figure A.4.1. Sulfate adsorption isotherm.

various regions of the United States such as the Southeast. These estimates can be compared with input-output budgets for those regions such as the northeastern United States that are considered to be in steady state.

4.5.4 Ion Exchange

Ion exchange and weathering replacement are hypothesized to be two important factors in determining base supply rate (Sections 3.4 Cation Exchange Processes and 4.5.2 Weathering Replacement). These paragraphs will discuss an approach for estimating the time to deplete the watershed exchangeable cation supply.

4.5.4.1 Approach

Soil cation exchange capacity (CEC) is defined as the total quantity of exchangeable cations (metallic and hydrogen) adsorbed on mineral surfaces. The percent base saturation (% BS) is defined as the fraction of exchange sites occupied by base cations (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}) (see Section 3.4, Cation Exchange Processes, Chapter 3). The % BS varies inversely with hydrogen ion concentration. Using measured % BS, one can theoretically "titrate" the soils to estimate the time required to deplete the base cations at present deposition levels. The salt effect (buffering by Al compounds) becomes important at lower % BS values of about 15% (Reuss and Johnson, 1985). Although, dependent upon other factors, these can be established. The time response can be computed assuming: (a) no (zero) external supply of base cations; (b) atmospheric inputs but no (zero) weathering supply; and (c) minimum weathering supply of base cations. The minimum weathering rates will be computed for different minerals using the lower range of fractional order dissolution rates cited by Schnoor and Stumm (1984) (see Section 4.6.4, Trickle-Down Model, Chapter 4, Part A).

4.5.4.2 Previous Applications

This specific approach has not been previously applied but it is similar to steady state model applications of Henriksen (1980, 1982), Wright (1983), and Schnoor (1983).

4.5.4.3 Advantages and Disadvantages

Advantages of this approach are:

- Base cation depletion rates can be estimated for various deposition rates.
- These estimates can be compared with estimates of cation supply from other soil processes such as mineral weathering.

The disadvantages of this approach are:

- Inasmuch as CEC and % BS are influenced by pH, these factors must be measured at soil pH, not the standard measurements at buffered pH 7 soil solution.
- Biological uptake, including preferential cation uptake, and other removal processes are not included

4.5.4.4 Expected Utility

Estimates of potential base cation depletion rates can be calculated for various regions of the United States. For systems in steady state with sulfate inputs, the base supply rate and exchangeable cation pool represents an important soil neutralization process.

4.5.5 Conclusions

Order of magnitude time estimates can be computed for each of the dynamic processes identified above. These processes, however, do not occur in isolation. These processes are highly interactive and influenced by other factors. The time estimates do indicate the relative importance of various soil processes in neutralizing acid deposition inputs but must be integrated for a holistic assessment. Dynamic models represent one approach for integrating these processes.

4.6 DYNAMIC SYSTEM MODELS

4.6.1 Definition

Dynamic system models simulate the response of a system through time. These models integrate time-varying inputs through a set of process formulations or equations to produce a time-varying trajectory or time series of output variables. Dynamic system models are defined by their integration of processes occurring within a system with respect to time.

4.6.2 Integrated Processes

The mechanisms controlling or influencing surface water chemistry (Figure B.2.7) are neither isolated nor static processes. The processes are highly interactive and vary over time scales from minutes to decades. Dynamic system models integrate these processes to simulate response of systems to acidic deposition through time. Dynamic models represent our present understanding of how multiple processes such as hydrologic flow paths, weathering replacement, anion retention, and base cation buffering interact through time to control surface water acidification.

4.6.3 General Requirements

The general requirements for most dynamic acidification models are similar because the processes incorporated in these models are similar. These general requirements are shown in Table A.4.1. Specific acidification models including data requirements are discussed in the following sections.

4.6.4 Trickle-Down Model

4.6.4.1 Purpose of Development (Objectives)

The Trickle-Down model was developed to perform acid precipitation assessments on a number of seepage lakes (lakes without any inlets or outlets) in the Upper Midwest. The objective of the modeling effort was to provide an "in-between" approach for acid precipitation assessments; that is, a model that is detailed enough to solve for alkalinity concentrations in surface water, soil, and groundwater, and yet simple enough to be run on a microcomputer using one master variable (alkalinity). Alkalinity (acid neutralizing capacity, ANC) was selected as the master variable because it represents the aggregate of all acid/base reactions that occur in the watershed. Thus, any reaction that occurs in the watershed (e.g., sulfate reduction, biomass synthesis, ammonia oxidation, or chemical weathering) must be formulated in terms of its effects on alkalinity via stoichiometry. The Trickle-Down was not developed to address questions involving the fate of any particular cation or anion. It cannot be used to address forest nutritional effects, but it can be used to calculate the alkalinity, pH, and aluminum concentrations of a lake using daily precipitation inputs as the driving variable. By adjusting the acidity of precipitation or the amount of dry deposition, the effects of various loading scenarios can be determined.

Table A.4.1. General requirements for dynamics watershed-surface water chemistry models.

1. Deposition

   - deposition chemistry
   - standard meteorological data

2. Watershed/Soil Physical Characteristics

   - watershed area
   - vegetative cover (by type)
   - catchment slopes
   - depth of permeable material
   - bulk density
   - porosity
   - grain size distribution

3. Soil Chemical Characteristics

   - cation exchange capacity (neutral salt)
   - % base saturation (neutral salt)
   - exchangeable bases
   - lime potential
   - Fe and Al potential
   - SO_4 adsorption isotherms
   - extractable SO_4
   - organic content
   - pH
   - pCO_2
   - mineralogy

4. Lake Physical Characteristics

   - lake area
   - mean lake depth
   - maximum lake depth
   - secchi depth

5. Surface Water Chemistry

   - pH
   - alkalinity
   - acidity
   - base cations (Mg, Ca, Na, K)
   - strong acid anions (SO_4, NO_3, Cl)
   - Al
   - DOC
   - DIC
   - color
   - specific conductance

4.6.4.2 Conceptual Basis

The Trickle-Down model is based on the principle of continuity for alkalinity -- a mass balance approach. The key processes considered are chemical weathering, ion exchange, and hydrologic flow paths.

4.6.4.2.1 Key Processes and Levels of Parsimony

Chemical weathering is a key process on which this research has focused. Based on bar diagrams of water chemistry, it can be shown that the predominant watershed reaction that modifies precipitation chemistry is the release of cations (Ca^{+2}, Mg^{+2}, Na^{+}, K^{+}) coupled with base production and the possible formation of bicarbonate alkalinity ($OH^{-} + CO_2 = HCO_3^{-}$). This is true for the vast majority of watersheds in the Upper Midwest and Northeast U.S. where sensitive lakes have been studied. Weathering and ion exchange phenomena can be important processes in sediment-water as well as soil-water interactions, so the kinetics discussed here apply also to the sediment-water interface.

Garrels and Christ (1965) were two of the first to demonstrate that congruent and incongruent dissolution of minerals inevitably leads to a consumption of X equivalents of acid and the production of X equivalents of cations. Generally, calcium ions are the most readily dissolved component of rocks and minerals. For example, for the calcium-plagioclase mineral anorthite, incongruent dissolution results in the release of Ca^{+2} and the formation of a clay residual, kaolinite.

$$\begin{array}{lcll}
CaAl_2Si_2O_8 \text{ (anorthite)} + 2\,H^{+} & \longrightarrow & 2\,Al(OH)_{3(s)} + Ca^{+2} + 2\,H_4SiO_4 & (1) \\
2\,Al(OH_{3(s)} + 2H_4SiO_4 & \longrightarrow & Al_2Si_2O_5(OH)_4 \text{ (kaolinite)} + 5\,H_2O & (2) \\
\hline
\text{anorthite} + 2\,H^{+} & \longrightarrow & Ca^{+2} + \text{kaolinite} + 5\,H_2O & (3)
\end{array}$$

The stoichiometry of mineral dissolution equations provides the link between cation release and equivalent alkalinity generation within a watershed.

The dependency of mineral weathering on hydrogen ion activity in solution can be demonstrated using surface coordination chemistry as in Stumm et al. (1983) and Schnoor and Stumm (1984). It is possible to express the rate of mineral dissolution in terms of the hydrogen ion concentration in bulk solution

$$\text{Rate} \propto [H^+]^m \qquad (4)$$

in which m is the fractional order dissolution rate. For aluminum oxide dissolution, Stumm et al. (1983) have shown that m = 0.4 (fractional order). In addition to theoretical arguments, experimental evidence exists to validate that equation (4) is appropriate for a wide variety of minerals (Table A.4.2).

But hydrogen ion attack on minerals (hydrolysis) is not the only means of mineral dissolution. Other ligands, such as the sulfate anion or organics in soil solution, are known to accelerate the dissolution of minerals. This process, too, can be viewed as a surface coordination reaction.

The two types of mineral dissolution (hydrolysis and ligand attack) give rise to mixed kinetics overall. These reactions have a rate-determining step involving surface complexes, and the kinetics are given by equation (5), in which represents the mineral surface, A is the divalent anion ligand (e.g., oxalate or sulfate), z is the charge of the central metal cation, and k_1 and k_2 are rate constants.

$$\text{Rate} = k_1 [\exists\text{-}OH_2{}^+]^z + k_2[\exists\text{-}AH] \qquad (5)$$

The rate of mineral dissolution is related to the degree of protonation of the surface (or H^+ ion in bulk solution) and to the degree of ligand sorption (or ligand concentration in bulk solution).

Analogous weathering kinetics are discussed in Schnoor anod Stumm (1984) and included in the Trickle-Down model.

Table A.4.2. Reaction order for the rate of dissolution of minerals by acids.

Mineral	Formula	Solution	Rxn. Order	Reference
Dolomite	$(Ca,Mg)CO_3$	HCl	$[H^+]^{0.5}$	Busenberg and Plummer (1982)
Bronzite	$(Mg,Ca)SiO_3$	HCl	$[H^+]^{0.5}$	Grandstaff (1977)
Enstatite	$MgSiO_3$	HCl	$[H^+]^{0.8}$	Schott *et al.* (1981)
Diopside	$CaMgSi_2O_6$	HCl	$[H^+]^{0.7}$	Schott *et al.* (1981)
K-Feldspar	$KAlSi_3O_8$	Buffer	$[H^+]^{0.33}$	Wollast (1967)
Iron Hydroxide	$Fe(OH)_3$-Gel	Various Acids	$[H^+]^{0.48}$	Furuichi *et al.* (1969)
Aluminum Oxide	$-Al_2O_3$	HCl	$[H^+]^{0.4}$	Stumm *et al.* (1983)

$$\text{Rate} = k_h \left[\frac{H^+}{H^+_{ref}} \right]^m + k_o \qquad (6)$$

in which k_h = hydrolysis rate constant, eq/ha-yr

m = fractional reaction order for hydrolysis

k_o = rate constant for ligand attack, eq/ha-yr

H^+_{ref} = reference hydrogen ion activity, eq/l.

Attack by hydrogen ions is fractional order -- a fact with profound implications for "acid rain" assessments. To the extent that acidic deposition increases hydrogen ion activity in soils and sediments, we may expect increases in the rate of leaching and weathering. If the H^+ ion activity doubles, the weathering will increase, but less than a doubling, due to the fractional order kinetics that apply. Thus, acid precipitation is only partially compensated by increases in chemical weathering.

The implication of equation (5) is that sulfate ion may speed the rate of chemical weathering in addition to the hydrogen ion attack of H_2SO_4. Sulfate is a ligand, and equations (5-6) apply here as well. Furthermore, this requires that soils that are well buffered with respect to pH by CO_2 supersaturation and by organic acids (and which otherwise would not be much affected by acid precipitation) may still be leached by sulfate. The mobile anion concept would apply.

The Trickle-Down model uses a kinetic approach. No primary minerals are at chemical equilibrium with respect to the aquatic and terrestrial environment at these locations with the possible exception of gibbsite. Therefore, a kinetic approach makes sense. Even ion exchange is not likely to be at chemical equilibrium during precipitation events (Ardakani and McLaren, 1977), and especially considering the possibility of macropore flow.

Neutralization processes that occur internally to the lake are presently calculated in the Trickle-Down model as a zero-order input of alkalinity at the sediment-water interface. The rate constant for internal neutralization is determined from model calibration with field data.

A weathering process that was recently added to the Trickle-Down Model and which is presently being tested with data from Lakes Clara and Vandercook is the aluminum speciation submodel. Aluminum concentrations are derived from alkalinity and pH output variables of the Trickle-Down model and are calculated assuming saturation of microcrystalline gibbsite.

Ion exchange is another key process that is included in the Trickle-Down model. Cation exchange reactions can occur between hydrogen ions and base cations producing the same net effect as mineral dissolution but with more rapid kinetics. Using a calcium base exchange site (-R) as an example:

$$\text{Ca-R} + 2\ \text{H}^+ \longleftrightarrow \text{H}_2\text{-R} + \text{Ca}^{+2} \quad (7)$$

The kinetics of this reaction are assumed to be directly proportional to the sum of exchangeable bases in the upper soil horizons.

$$\frac{d(Va)}{dt} = k\ M\ V_e\ (r_o - r) \quad (8)$$

A = alkalinity concentration, eq/m^3

V = water column within the compartment, m^3

t = time, days

k = ion exchange rate constant, day^{-1}

M = bulk density of soil, kg/m^3

V_e = total environmental volume of the compartment, m^3

r_o = initial sum of exchangeable bases, eq/kg

r = exchangeable base depletion, eq/kg

The rate constant, k, can be made a function of hydrogen ion or neutral salt concentration to the fractional power, temperature, mean soil particle size, or flow rate through the soil, but only hydrogen ion dependence has been tested so far. The exchangeable base depletion term, r, allows estimation of delayed response systems. As r increases during the course of a long-term simulation, the base exchange rate decreases until such time as all the exchangeable bases are depleted ($r_0 - r = 0$). Mineral dissolution (chemical weathering) would continue, and it could serve to replenish the depleted exchangeable bases. This is a mechanism that is easily facilitated in the Trickle-Down model, and plans are for it to be implemented in the model code. To assess delayed response systems, it will be necessary to know the size and quantity of readily weatherable minerals (e.g., feldspars, silicates, pyroxenes, and amphiboles) in the soil horizons.

Hydrologic processes are another key element of the Trickle-Down model. The hydrologic submodel was developed primarily by Banwart (1983). It is somewhat similar to that reported by Chen et al. (1982). It includes snowpack hydrology, overland flow or stream flow, infiltration, interflow, and groundwater exchange between the lake and the groundwater table aquifer. The existing version of the Trickle-Down model has been developed and tested for seepage lakes, and application to drainage lakes would require further model development.

4.6.4.2.2 Resolution

The model can be resolved into its temporal and spatial increments. For the temporal scale, the model requires daily precipitation inputs and can be used to simulate many decades. It has executed for 50 years using a three-year record repetitively with complete stability and convergence. The time step is usually 0.1 days, but it can approach 1.0 days in most circumstances with acceptable accuracy.

Spatial -- The compartments are divided into horizontal slices of variable thickness: a snowpack compartment, approximately a one-foot upper soil horizon, and a variable unsaturated zone, water table aquifer, and lake compartment. Storage of water in each compartment occurs during and following precipitation events, so the water volume of each compartment is variable over time for a given watershed.

4.6.4.2.3 Assumption

The key assumptions of the model are listed below.

1. Chemical weathering and ion exchange are the main processes that neutralize acidic deposition and control water chemistry.
2. The rates of these reactions are dependent on the fractional order hydrogen ion activity in solution, the mineralogy of the soils, base exchange capacity, and factors determining the hydrologic flow paths (soil permeability, hydraulic conductivity, and depth to bedrock).
3. Sulfate retention in the watersheds to which the model has been applied is relatively small and can be neglected.
4. Free monomeric aluminum concentrations can be estimated from microcrystalline gibbsite solubility in soil waters.

4.6.4.3 Model Inputs

The total model inputs are presented in Appendix A and summarized in Table A.4.3. Theoretical thermodynamic constants for carbonate equilibrium and aluminum speciation are internal to the model and were obtained from the MINTEQ (Felmy et al., 1983) geochemistry model developed at Battelle Pacific Northwest

Table A.4.3. Trickle-Down model inputs by category.

---

1. Deposition/Meteorology
   - -- Precipitation quantity and duration
   - -- Rainfall alkalinity
   - -- Dry fall alkalinity
   - -- Air temperature
   - -- Atmospheric partial pressure of CO_2

2. Watershed/Soil Physical Characteristics
   - -- Area
   - -- Depth to bedrock
   - -- Volume of soil Comparment
   - -- Porosity
   - -- Bulk density

3. Soil Chemistry
   - -- Weathering reaction rates
   - -- Sum of base cations
   - -- Base initially consumed
   - -- Supersaturated partial pressure of CO_2
   - -- Initial alkalinity
   - -- F concentration
   - -- SO_4 concentration
   - -- pKa for organics - H
   - -- pK for organics - Al

4. Hydrology
   - -- Pan evaporation coefficients
   - -- Lateral flow rate constant
   - -- Initial soil moisture content
   - -- Length of seepage flow path
   - -- Hydraulic gradient
   - -- Distance along watershed boundary normal to export/import flow path
   - -- Evapotranspiration depth

5. Lake
   - -- Area
   - -- Average depth
   - -- Initial elevation, volume
   - -- Stage/volume relationship
   - -- Outlet height, configuration
   - -- Depth to groundwater at various stages
   - -- Pan evaporation coefficient
   - -- Lake bed permeability
   - -- Sediment alkalinity transport coefficient
   - -- Initial alkalinity
   - -- TOC concentrations

Laboratory. Vertical permeability and weathering reaction rates are initially estimated from literature values but are checked or modified by model calibration. All other input variables must be measured in the field or obtained from maps.

4.6.4.4 Model Outputs

The program is run on a PRIME 750 computer with batch-remote entry. Output consists of an echo-print of all input data, followed by a tabular output of flows, alkalinity concentrations, and pH values at each print interval (say, 10 day increments) for each compartment (snow, soil, unsaturated zone, lake, and groundwater). An annual budget for sources and sinks of alkalinity is printed. Aluminum species concentrations (free aluminum, Al-OH complexes, Al-F complexes, Al-SO_4 complexes, Al-organic complexes, and total Al) are given in the last table of the output.

A graphical output is also possible using the software program TELEGRAF and the ZETA plotter. Some examples of the graphical output are shown in Figures A.4.2 - A.4.8.

4.6.4.5 Sensitivity Analyses

Sensitivity analyses for three important inputs to the Trickle-Down model are presented in Figures A.4.2 - A.4.5 for Lake Vandercook, a seepage lake in Vilas County, Wisconsin. Figure A.4.2 shows that if the total acid loading (pH of precipitation = 4.6 with 20% of total falling as dry deposition) doubles, the lake becomes considerably more acidic in a relatively short period of time. Figure A.4.3 is an analysis of the most sensitive weathering rate constant in the model, P, the sediment neutralization rate. Vandercook Lake obtains approximately 76 percent of its alkalinity from internal processes (weathering,

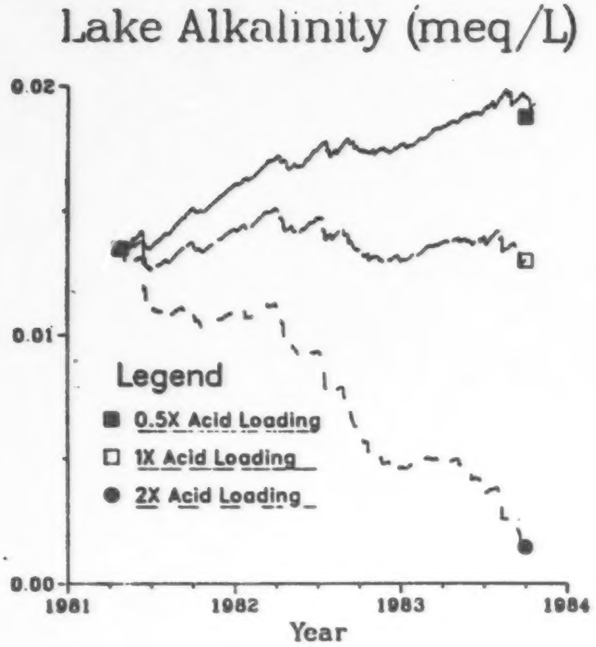

Figure 1. Sensitivity analysis on total acid loading for Lake Vandercook alkalinity concentration

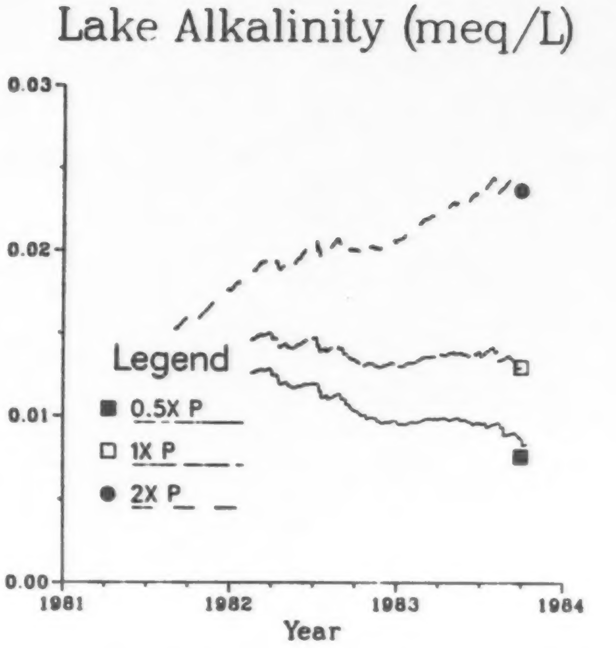

Figure 2. Sensitivity analysis on sediment/water neutralization rate for Lake Vandercook alkalinity concentration

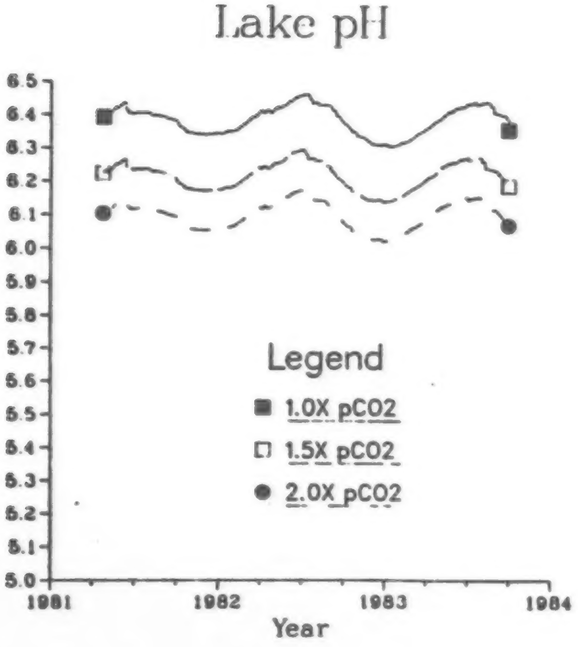

Figure 3. Sensitivity analysis on the partial pressure of carbon dioxide for Lake Vandercook pH

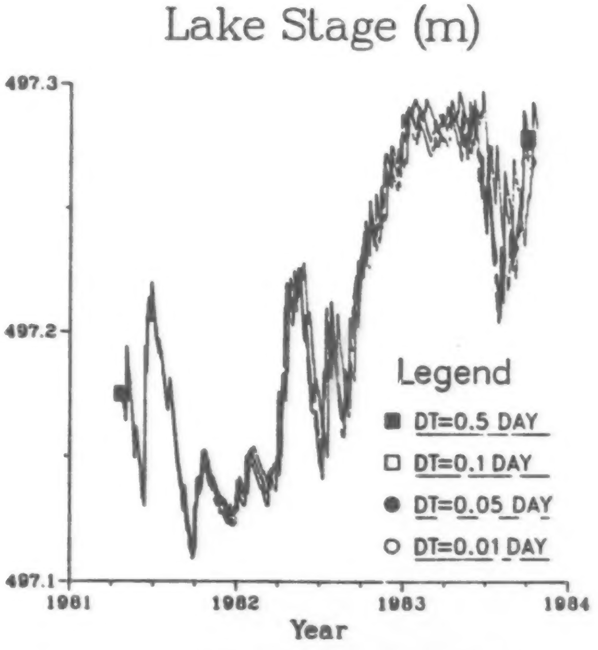

Figure 4. Numerical sensitivity of time-step on the calculation of lake stage for Vandercook Lake

Figures A.4.2 - A.4.5

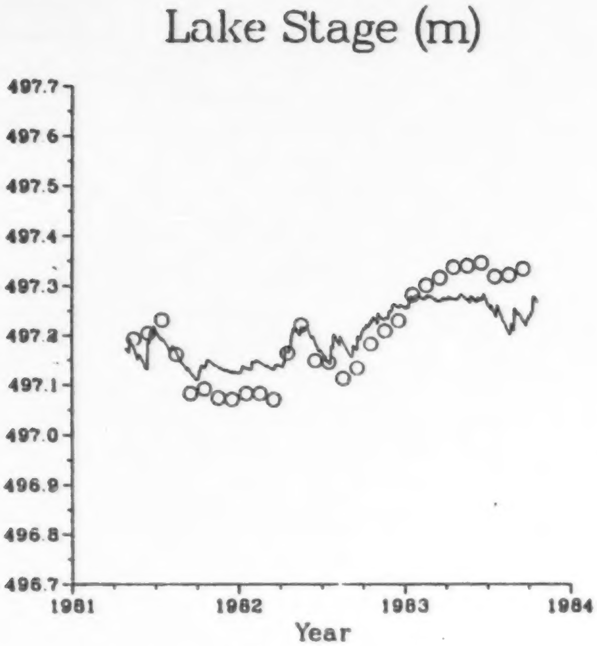

Figure 5. Results of hydrologic model calibration of lake stage for Vandercook Lake

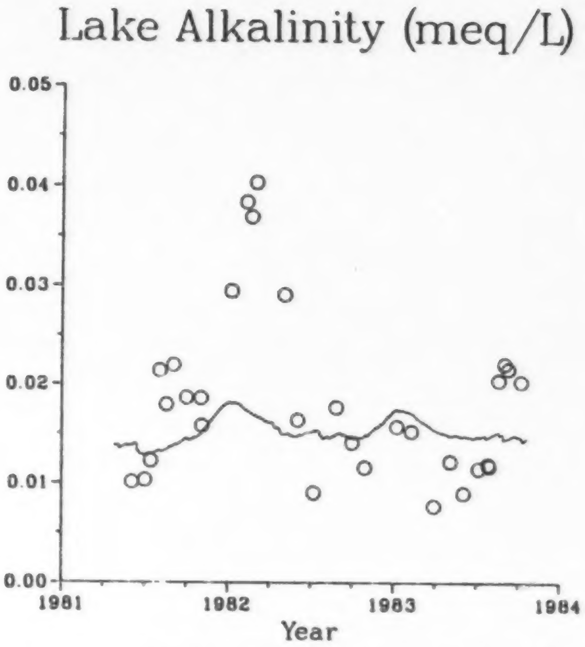

Figure 6. Results of alkalinity model calibration for Vandercook Lake

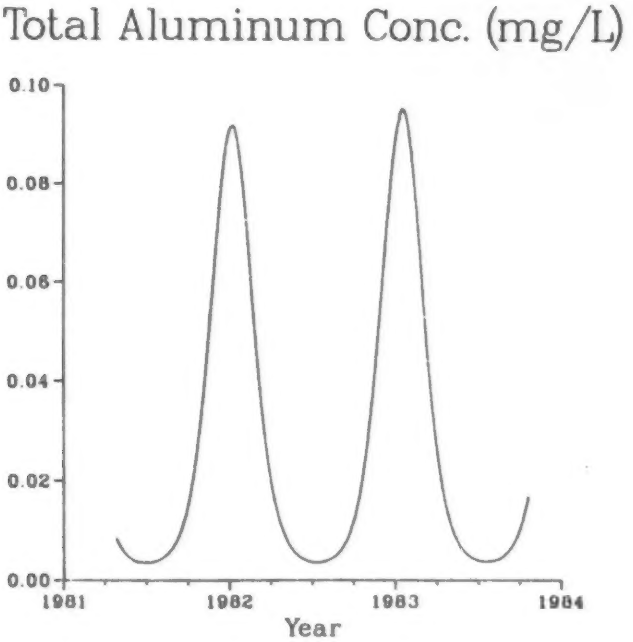

Figure 7. Results of total aluminum concentration from the Al speciation sub-model for Lake Vandercook

Figures A.4.6 - A.4.8

ion exchange, sulfate reduction). Thus, the sensitivity analysis shows that a halving or doubling of the internal neutralization rate greatly affects the alkalinity concentration in the lake. Bar diagrams of water chemistry indicate that chemical weathering or ion exchange, particularly in the winter at cold temperatures and high CO_2 concentrations under ice, are responsible for much of this internal alkalinity generation. Figure A.4.4 shows that the partial pressure of carbon dioxide that is assumed for the lake is very important to the resulting pH. There are indications that pCO_2 increases under ice cover. Figure A.4.4 is a different type of sensitivity analysis showing that the numerical technique is convergent with small errors generated even at large time steps.

4.6.4.6 Model Testing Application

4.6.4.6.1 Applications

The model presented here has been applied to Lakes Clara and Vandercook in northcentral Wisconsin. The project was a joint effort by the U.S. EPA Environmental Research Laboratory--Duluth, the Wisconsin Department of Natural Resources (Rhinelander), the U.S. Geological Survey (Madison), and the University of Iowa. Input data sets are available from the University of Iowa, and the water chemistry data base is the U.S. EPA ERL-Duluth Deposition Gradient-Susceptibility Database (October 1984).

The Trickle-Down model was first applied to Omaday Lake in northeastern Minnesota. This earlier version of the model did not contain a hydrologic submodel nor an aluminum speciation submodel. Flow rates were estimated on a daily basis for each compartment and used as input to the model. Also, annual average flows and rate constants were used in a 20-year simulation of worst case conditions. The results were reported in Schnoor et al. (1984), and a reprint is provided in the Appendix A-2.

4.6.4.6.2 Calibration and Predictions

Three years of data (1981-84) were used for model testing and calibration for Lakes Clara and Vandercook. Predictions were made for 25-year simulations using a three-year input record repetitively. Results are shown for Lake Vandercook in Figures A.4.6 - A.4.8.

Figure A.4.6 shows the calibration for lake stage. In calibration of the hydrology, the hydraulic conductivities of the compartments (soil, unsaturated zone, and water table aquifer) are varied in order to obtain a close agreement between field measurements of well stage and lake stage with time. Figure A.4.6 shows agreement within about 0.1 m of measured lake stage values -- this represents an error in lake volume of less than three percent.

Figure A.4.7 gives the alkalinity calibration results. Using alkalinity observations from the lake and groundwater, it was possible to determine weathering and ion exchange rate constants in the model. These were in good agreement with overall weathering rates obtained in similar calibrated watersheds. (The cause of the large alkalinity peak in early 1982 is unknown at this time and was not matched by model output. A possible explanation is weathering of newly delivered allochthonous material from large antecedent rainfall events with a 100-year recurrence interval.)

Figure A.4.8 reports the results of the total aluminum concentration in the lake from the aluminum speciation model. Although the aluminum concentration is not large, it shows a distinct seasonal trend to high concentrations during winter. Solubility of gibbsite increases at low temperature and is responsible for the seasonality. Results are in good agreement with the few field measurements available.

4.6.4.6.3 Results

Results of the calibration effort were acceptable and (except for the alkalinity peak in early 1982) always within one standard deviation of variability in field data. Long-term predictions to the year 2005 indicate that Lakes Clara and Vandercook should retain a small amount of alkalinity provided that present loading conditions continue.

4.6.4.7 Model Utility

The model can be used to determine seasonal and long-term risk of acidification to intensively studied seepage lakes. It can address a myriad of questions posed, such as:

1. What will be the time series of lake pH, alkalinity, and aluminum for any increase or decrease in acid loading? This relates to fisheries questions.
2. What would be the long-term effect of constant loading (direct versus delayed response)?
3. What would be the effect of liming the lake? How long would the effect last?
4. What is the relative role of internal versus external alkalinity reactions to the lake? Seepage lakes seem to be dominated by internal lake processes.

4.6.5 Model of Acidification of Groundwater in Catchments (MAGIC)

This synopsis of the MAGIC model is based on Cosby _et al_. (1984, 1985a, b). The MAGIC model is described in detail in Appendix A-2.

4.6.5.1 Purpose of Development (Objectives)

The major purpose of this research was to develop a physically based, intermediate complexity model of catchment water quality response to acidic deposition. Three specific objectives included:

1. to demonstrate the particular adequacy of the model by calibrating and applying it to an individual catchment and analyzing the results;
2. to demonstrate the general adequacy of the model by determining the relative importance (identifiability) of the lumped processes included in the model;
3. to be parsimonious in selecting processes for inclusion in the model so that the final product could be based on a heuristic tool for understanding the influences of the assumed model processes on surface water acidification.

4.6.5.2 Conceptual Basis

The most serious effects of acidic deposition on catchment surface water quality are thought to be decreased pH and alkalinity and increased base cation (i.e., Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+}) and aluminum concentrations. A lumped approach to modeling catchments was used that incorporated a relatively small number of important soil processes (i.e., processes that could be treated by average soil properties) to produce these responses. In two papers, Reuss (1980, 1983) proposed a simple system of reactions describing the equilibrium between dissolved and adsorbed ions in the soil-soil water system. Reuss and Johnson

(1985) expanded this system of equations to include the effects of carbonic acid resulting from elevated CO_2 partial pressure in soils. Chemical conditions in the soil were assumed to be uniform throughout the catchment being modeled. Surface water chemistry was determined by the model by "removing" the soil water from contact with the soil, allowing the excess CO_2 to degas to the atmosphere with subsequent precipitation of aluminum hydroxides as the solution pH indreased.

Reuss and Johnson (1985) demonstrated that large changes in surface water chemistry would be expected as either CO_2 or strong acid anion (i.e., SO_4^{2-}, NO_3^-) concentrations varied in the soil water. Their conceptual approach permits a wide range of observed catchment responses to be theoretically produced by a rather simple system of soil reactions. The MAGIC model has its roots in the Reuss-Johnson conceptual system, but has been expanded from their simple two component (Ca-Al) system to include other important cations and anions in catchment soil and surface waters identified by Galloway *et al.* (1983).

The model is composed of:

- A set of equilibrium equations that quantitatively describe the equilibrium soil processes and the chemical changes that occur as soil water enters the stream channel.
- A set of mass balance equations that quantitatively describe the catchment input-output relationships for base cations and strong acid anions in precipitation and streamwater.
- A set of definitions that relate the variables in the equilibrium equations to the variables in the mass balance equations (Table A.4.4).

Inasmuch as the model assumes that stream water chemistry is determined by reactions taking place in the soils and rocks within a catchment, it was titled MAGIC (Model of Acidification of Groundwater In Catchments).

Table A.4.4 Summary of model equations, parameters and inputs. Braces denote activities, parentheses denote molar concentrations. An extended Debye-Huckel expression was used to convert molar concentrations to activities. Unit of other variables, parameters and inputs are given in the text.

Equilibrium Equations

Soil-water cation exchange reactions

1. $E_{Al} + E_{Ca} + E_{Mg} + E_K + E_{Na} = 1$

2. $BS = E_{Ca} + E_{Mg} + E_K + E_{Na} = 1-E_{Al}$

3. $$\frac{(Ca^{2+})^3 E_{Al}^2}{(Al^{3+})^2 E_{Ca}^3} = S_{AlCa}$$

4. $$\frac{(Na^+)^2 E_{Ca}}{(Ca^{2+}) E_{Na}^2} = S_{CaNa}$$

5. $$\frac{(Na^+)^2 E_{Mg}}{(Mg^{2+}) E_{Na}^2} = S_{MgNa}$$

6. $$\frac{(Na^+) E_K}{(K^+) E_{Na}} = S_{KNa}$$

Inorganic aluminum reactions

7. $$\frac{(Al^{3+})}{(H^+)^3} = K_{Al}$$

8. $$\frac{(Al(OH)^{2+})(H^+)}{(Al^{3+})} = K_{Al_1}$$

9. $$\frac{(Al(OH)_2^+)(H^+)^2}{(Al^{3+})} = K_{Al_2}$$

10. $$\frac{(Al(OH)_3^0)(H^+)^3}{(Al^{3+})} = K_{Al_3}$$

11. $$\frac{(Al(OH)_4^-)(H^+)^4}{(Al^{3+})} = K_{Al_4}$$

12. $$\frac{(AlF^{2+})}{(Al^{3+})(F^-)} = K_{Al_5}$$

13. $$\frac{(AlF_2^+)}{(Al^{3+})(F^-)^2} = K_{Al_6}$$

14. $$\frac{(AlF_3^0)}{(Al^{3+})(F^-)^3} = K_{Al_7}$$

15. $$\frac{(AlF_4^-)}{(Al^{3+})(F^-)^4} = K_{Al_8}$$

16. $$\frac{(AlF_5^{2-})}{(Al^{3+})(F^-)^5} = K_{Al_9}$$

17. $$\frac{(ALF_6^{3-})}{(Al^{3+})(F^-)^6} = K_{Al_{10}}$$

18. $$\frac{(Al(SO_4)^+)}{(Al^{3+})(SO_4^{2-})} = K_{Al_{11}}$$

19. $$\frac{(Al(SO_4)_2^-)}{(Al^{3+})(SO_4^{2-})^2} = K_{Al_{12}}$$

Inorganic carbon reactions

20. $$\frac{(CO_2(aq))}{P_{CO2}} = K_{CO2_1}$$

21. $$\frac{(HCO_3^-)(H^+)}{(CO_2(aq))} = K_{CO2_2}$$

22. $$\frac{(CO_3^{2-})(H^+)}{(HCO_3^-)} = K_{CO2_3}$$

Dissociation of Water and Ionic balance

23. $(H^+)(OH^-) = K_w$

24. $$\begin{aligned}&(H^+) - (OH^-) + 2(Ca^{2+}) + 2(Mg^{2+}) + (K^+) + (Na^+) + 3(Al^{3+}) + 2(Al(OH)^{2+}) + (Al(OH)_2^+) - (Al(OH)_4^-)\\ &+ 2(AlF^{2+}) + (AlF_2^+) - (AlF_4^-) - 2(AlF_5^{2-}) - 3(AlF_6^{3-}) + (Al(SO_4)^+) - (Al(SO_4)_2^-) - (Cl^-) - (F^-)\\ &- (NO_3^-) - 2(SO_4^{2-}) - (HCO_3^-) - 2(CO_3^{2-}) = 0\end{aligned}$$

Table A.4.4.(continued)

Variables

base cations: (Ca^{2+}), (Mg^{2+}), (Na^{+}), (K^{+})

strong acid anions: (Cl^{-}), (F^{-}), (NO_3^{-}), (SO_4^{2-})

inorganic aluminum species: (Al^{3+}) $(Al(OH)^{2+})$, $(Al(OH)_2^{+})$, $(Al(OH)_3^{0})$, $(Al(OH)_4^{-})$, (AlF^{2+}), (AlF_2^{+}), (AlF_3), (AlF_4^{-}), (AlF_5^{2-}), (AlF_6^{3-}), $(Al(SO_4)^{+})$, $(Al(SO_4)_2^{-})$

inorganic carbon species: $(CO_2(aq))$, (HCO_3^{-}), (CO_3^{2-}),

dissociation of water: (H^{+}), (OH^{-})

exchangeable cation fractions: E_{Ca}, E_{Mg}, E_K, E_{Na}, E_{Al}

base saturation: BS

total ion amounts: Ca_T, Mg_T, Na_T, K_T, SO_{4T}, Cl_T, NO_{3T}, F_T

adsorbed sulfate: E_S

alkalinity: ALK

sums of base cations and strong acid aanions: SBC, SSA

Parameters

Thermodynamic equilibrium constants (functions of temperature):

K_{Al_1}, K_{Al_2}, K_{Al_3}, K_{Al_4}, K_{Al_5}, K_{Al_6}, K_{Al_7}, K_{Al_8}, K_{Al_9}, $K_{Al_{10}}$, $K_{Al_{11}}$, $K_{Al_{12}}$, K_{CO2_1}, K_{CO2_2}, K_{CO2_3}, K_w

Lumped parameters (functions of catchments):

selectivity coefficients: S_{AlCa}, S_{CaNa}, S_{MgNa}, S_{KNa}

aluminum solubility constant: K_{Al}

soil chemical properties: C, E_{mx}, CEC

soil physical properties: SP, V

Inputs (functions of time)

streamflow: Q

atmospheric deposition: F_{Ca}, F_{Mg}, F_{Na}, F_K, F_{SO4}, F_{Cl}, F_{NO3}, F_F

primary mineral weathering: W_{Ca}, W_{Mg}, W_{Na}, W_K, W_{SO4}, W_{Cl}, W_{NO3}, W_F

partial pressure CO_2: P_{CO2}

soil water and streamwater temperatures
(for correction of thermodynamic constants)

Table A.4.4 (continued)

Mass Balance Equations

1. $dCa_T/dt = F_{Ca} + W_{Ca} - Q*2*(Ca^{2+})$
2. $dMg_T/dt = F_{Mg} + W_{Mg} - Q*2*(Mg^{2+})$
3. $dNa_T/dt = F_{Na} + W_{Na} - Q*(Na^{+})$
4. $dK_T/dt = F_K + W_K - Q*(K^{+})$
5. $dSO_{4T}/dt = F_{SO4} + W_{SO4} - Q*2*((SO_4^{2-}) + (Al(SO_4)^{+}) + 2*(Al(SO_4)_2^{-})$
6. $dCl_T/dt = F_{Cl} + W_{Cl} - Q*(Cl^{-})$
7. $dNO_{3T}/dt = F_{NO3} + W_{NO3} - Q*(NO_3^{-})$
8. $dF_T/dt = F_F + W_F - Q*((F^{-}) + (AlF^{2+}) + 2(AlF_2^{+}) + 3(AlF_3^{0}) + 4(AlF_4^{-}) + 5(AlF_5^{2-}) + 6(AlF_6^{3-}))$

Definitions

Sulfate adsorption

1. $E_S = E_{mx}*2(SO_4^{2-})/(C + 2(SO_4^{2-}))$

Alkalinity

2. $ALK = (HCO_3^{-}) + 2(CO_3^{2-}) + (OH^{-}) - (H^{+}) - 3(Al^{3+}) - 2(Al(OH)^{2+}) - (Al(OH)_2^{+}) + (Al(OH)_4^{-}) - 3(AlF^{2+})$
$- 3(AlF_2^{+}) - 3(AlF_3^{0}) - 3(AlF_4^{-}) - 3(AlF_5^{2-}) - 3(AlF_6^{3-}) - 3(Al(SO_4)^{+}) - 3(Al(SO_4)_2^{-})$

Total ion amounts

3. $Ca_T = SP*CEC*E_{Ca} + 2*V*(Ca^{2+})$
4. $Mg_T = SP*CEC*E_{Mg} + 2*V*(Mg^{2+})$
5. $Na_T = SP*CEC*E_{Na} + V*(Na^{+})$
6. $K_T = SP*CEC*E_K + V*(K^{+})$
7. $SO_{4T} = SP*E_S + 2*V*((SO_4^{2-}) + (Al(SO_4)^{+}) + 2(Al(SO_4)_2^{-}))$
8. $F_T = V*((F^{-}) + (AlF^{2+}) + 2(AlF_2^{+}) + 3(AlF_3^{0}) + 4(AlF_4^{-}) + 5(AlF_5{}^{2-}) + 6(AlF_6{}^{3-}))$
9. $Cl_T = V*(Cl^{-})$
10. $NO_{3T} = V*(NO_3^{-})$

Sums of Aqueous Base Cation and Strong Acid Anion Concentrations

11. $SBC = 2(Ca^{2+}) + 2(Mg^{2+}) + (Na^{+}) + (K^{+})$
12. $SSA = 2(SO_4^{2-}) + (Cl^{-}) + (NO_3^{-}) + (F^{-})$

4.6.5.2.1 Key Processes and Levels of Parsimony

The physical basis of the model is developed from general agreement as to which catchment soil processes are important in mitigating the effects of acidic deposition on surface water quality (NAS, 1984). The soil processes are:

1. anion retention by catchment soils (e.g., soil sulfate adsorption);
2. cation exchange by catchment soils;
3. alkalinity generation by carbonic acid dissociation;
4. dissolution of aluminum minerals in catchment soils;
5. mineral weathering replacement of cations.

An important characteristic of the model is the aggregated or "lumped" parameterization of these processes. There are two aspects of modeling large scale heterogeneous catchments that must be considered when using a lumped modeling approach -- process aggregation and spatial aggregation. Process aggregation concerns the degree to which the multitude of chemical processes that occur in a catchment can be represented by simpler conceptualizations of these processes. The processes that are included in the model are primarily generalizations of the interactions between soil and soil water.

Spatial aggregation concerns the scales of spatial heterogeneity in a catchment and the extent to which this spatial heterogeneity can be neglected. The model was not developed with the intention of describing the distributed nature of chemical processes in the catchment. Instead, the model was developed to determine if the net effects of soil processes on streamwater chemistry could be viewed as occurring in a single soil compartment with uniform characteristics.

As implemented in its simplest form, the model is a two compartment representation of a catchment. Atmospheric deposition enters the soil compartment and the equilibrium equations are used to calculate soil water chemistry. The water is then routed to the stream compartment and the appropriate equilibrium equations are reapplied to calculate streamwater chemistry.

4.6.5.2.2 Resolution

Model resolution includes both spatial and temporal resolution. MAGIC spatially represents a catchment as being horizontally and vertically homogeneous or uniform. If a catchment has extensively developed A and B horizons in the soil and the soil processes are different in the two horizons, the model can be reconfigured using three compartments (i.e., two soil compartments and the stream compartment). The temporal resolution is variable but generally ranges from monthly to annual time estimates. Use of MAGIC at finer time scales of daily or hourly resolution (i.e., episodic events) is presently being investigated.

4.6.5.2.3 Assumptions

Some of the major assumptions in MAGIC include:

1. Soil processes identified by the NAS (1984) are the important processes influencing the effects of acidic deposition on surface water chemistry.
2. Only a few processes control gross system behavior and these are incorporated in the model.
3. Spatially heterogeneous watersheds can be represented assuming uniform soil properties for the catchment.
4. Chemical properties and processes can be assumed to be uniform with soil depth in a given compartment.
5. Atmospheric inputs are uniform over the catchment.

6. All water entering a catchment flows through the soil before entering the receiving body.
7. Sulfate is the dominant acidifying constituent.
8. The cations (Al^{3+}, Ca^{2+}, Mg^{2+}, K^{+}, Na^{+}) are the only dissolved cations that can exchange between the soil solution and soil matrix.
9. Biological transformations such as sulfate or nitrate reductions are not significant.

4.6.5.3 Model Inputs

Model inputs can be classed in three categories: theoretical, estimated, and measured. Theoretical inputs include thermodynamic or stoichiometric constants derived or computed from theoretical relationships. Estimated inputs may be obtained from the literature, calculated from empirical relationships, or inferred from other values. Measured values include atmospheric and hydrologic inputs, laboratory and field measurements of rate constants, and coefficients.

4.6.5.3.1 Required Inputs

Required inputs for MAGIC are listed in Table A.4.4. There are 21 parameters in the equilibrium equations, of which 16 are thermodynamic constants and 5 are lumped parameters calibrated for the catchment being studied. The variation of soil pCO_2 with time is assumed to be known for the catchment (i.e., pCO_2 is treated as a model input). Given values of pCO_2 and the 21 parameters, the equilibrium equations can be solved for the values of all variables at a particular time if the values of eight of the variables are known for that time, i.e., there are 24 equations and 32 variables.

The values of eight variables that must be known to solve the equilibrium equations can be obtained by considering the input-output chemical mass balance of the catchment as a whole. The mass balance is applied to the total amounts of base cations and strong acid anions in the catchment. Inputs of these eight ions are by atmospheric deposition and primary mineral weathering and outputs are by streamwater losses. For each of the base cations and strong acid anions in the mdoel, a dynamic mass balance equation (Table A.4.4) can be written in the form:

$$dX/_T/dt = F_x + W_x - Q\ (X)\ n,$$

where X_T is the total amount of ion x in the catchment (eq/m^2), F_x is the atmospheric flux of that ion into the watershed (eq/m^2-time), W_x is the mineral weathering input of the ion (eq/m^2-time), Q is the volume flow of the streams, (X) is the total molar concentration (free plus complexes of the ion in streamwater), and n is the charge of the ion. Atmospheric, hydrologic, and weathering fluxes are inputs to the model and their temporal trajectories must be specified. Measured soil properties include physical characteristics [bulk density (SP), porosity (P), soil temperature (T), and depth of watershed soils (D)] and chemical characteristics [maximum sulfate adsorption capacity (E_{mx}), half-saturation constant of the adsorption process (C), and soil partial pressure of CO_2 (pCO_2)].

4.6.5.3.2 Minimum Input

If the initial system can be assumed to be at steady state (i.e., long-term predictions beginning in 1850-1900), then only the atmospheric inputs and model parameters/coefficients are required to compute the variable concentrations and initiate the model simulations. Because the model is particularly sensitive to some parameters (see 4.6.5.5), these parameters should be selected carefully if measured data are not available.

4.6.5.4 Model Output

Once initial conditions have been established, the equilibrium equations are solved for soil water and streamwater variable concentrations. These concentrations are used to calculate the streamwater output fluxes of the model such as total base cation and strong acid anion concentrations. The output from MAGIC can be obtained in three formats: tabular format, line printer time traces, or screen plots. The output variables are generally those shown in Table A.4.5 and Figure A.4.9, but the output format can be written to provide any input or output values entered or computed in the model.

4.6.5.5 Sensitivity Analyses

Regionalized sensitivity analysis (RSA) (Hornberger and Spear, 1981) was used to identify those ranges and/or combinations of parameters that produce acceptable predictions of soil properties when the model is driven by the observed stream chemistry. This procedure depends on the ability to construct a plausible model structure, estimate broad ranges of parameter values from limited field data or from the literature, and define the range of acceptable limits. Ranges of parameter values and definition of acceptable results were established from data on White Oak Run watershed in Virginia.

The RSA involves using Monte Carlo procedures to randomly select a set of parameter values from within designated ranges and solve the system of equations using this particular set of values. The result of each simulation run is then classified as either producing acceptable results (i.e., predicted soil properties within the range of discrete observations of those properties) or as

Table A.4.5. Typical output variables from MAGIC in tabular format.

```
VOLUME WEIGHTED CONDITIONS AT WHITE OAK RUN       FOR YEAR 1864 ARE:
               PRECIP      SOIL      WEATH    ATM DEP     EXCHAN      TOTAL
               MEQ/M3    MEQ/M3  MEQ/M2/Y  MEQ/M2/Y          %      MEQ/M2
CA              7.157    15.067       .000      7.873       .521   1000.700
MG              4.000    28.132     10.000      4.400       .972   1868.300
NA              5.000    18.725      4.000      5.500       .251    488.150
K               2.000    27.955     12.000      2.200       .784   1509.100
SBC            18.157    89.879     26.000     19.973      2.528   4866.250
SO4             8.082    22.792       .000     15.114     18.562   2186.500
CL              7.000    21.400      3.000      7.700       .000      9.630
NO3             8.000     3.600     -7.000      8.800       .000      1.620
F                .000      .179       .500       .000       .000       .464
SSA            23.082    47.972     -3.500     31.614     18.562   2198.214

                 SOIL    STREAM
PH              5.135     6.309
ALK            40.953    41.010
H               7.332      .491
AL              1.518      .001
HCO3           53.936    40.823
SUM PLUS      102.020    90.457
SUM MINUS     101.940    90.435
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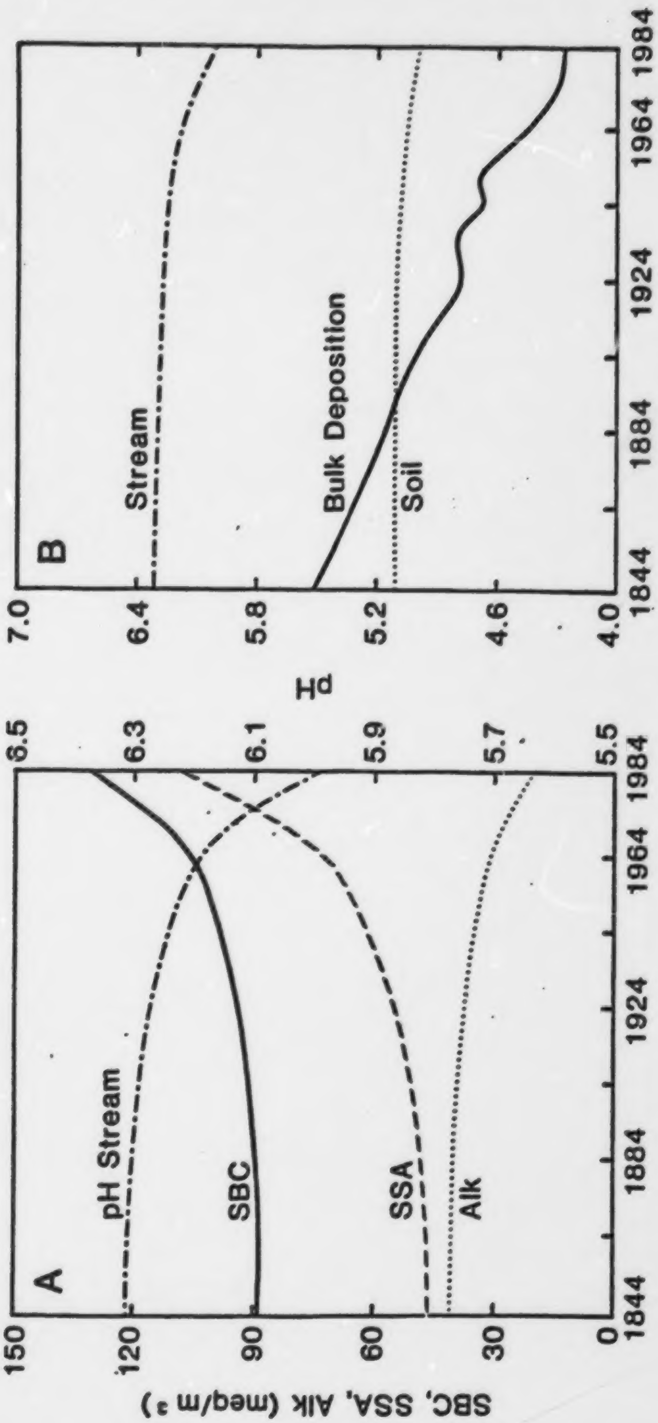

Figure A.4.9. Model reconstruction of streamwater and soil water chemistry for White Oak Run. A) Stream variables: sum of base cation concentrations (SBC), sum of strong acid anion concentrations (SSA), pH and alkalinity. B) pH of streamwater, soil water and precipitations.

not producing acceptable results. This procedure is repeated many times to give an accumulation of a set of values for the parameters for which results are acceptable and another set for which results are unacceptable. The key idea is then to identify the subset of physically or chemically meaningful parameters that appear to account for the acceptability of the results (Figure A.4.10). The distribution of parameter values associated with acceptable results is compared with the distribution of parameter values associated with unacceptable results. If the two distributions are not statistically different, the parameter is unimportant for simulating that particular set of results; if the two distributions differ significantly, the parameter is important for producing results within the specified ranges. The two distributions may reveal reduced ranges of values for the parameters that are favorable for adequate simulation.

Six parameter values were estimaed for the White Oak Run watershed application (S_{CaNa}, S_{MgNa}, S_{KNa}, S_{AlCa}, K_{Al}, and E_{Na}). To reduce the dimensionality of the problem, Ca and Mg were assumed to behave identically in soil cation exchange reactions (i.e., $S_{CaNa} = S_{MgNa}$).

The sensitivity of a given model result to a given parameter is determined by whether or not the probability distribution of parameters associated with acceptable results is significantly different than the distribution of parameters associated with unacceptable results. The Kilmogorov-Smirnov statistic and $p = 0.01$ were used to define differences between distributions. The sensitivities of each model prediction to those model parameters as determined by the RSA procedure are summarized in Table A.4.6 and A.4.7.

The MAGIC model also is sensitive to the seasonal variability in soil CO_2 concentrations, soil depth, and primary weathering rates. Limited data exist for all three factors. Soil CO_2 concentrations have been measured on a few

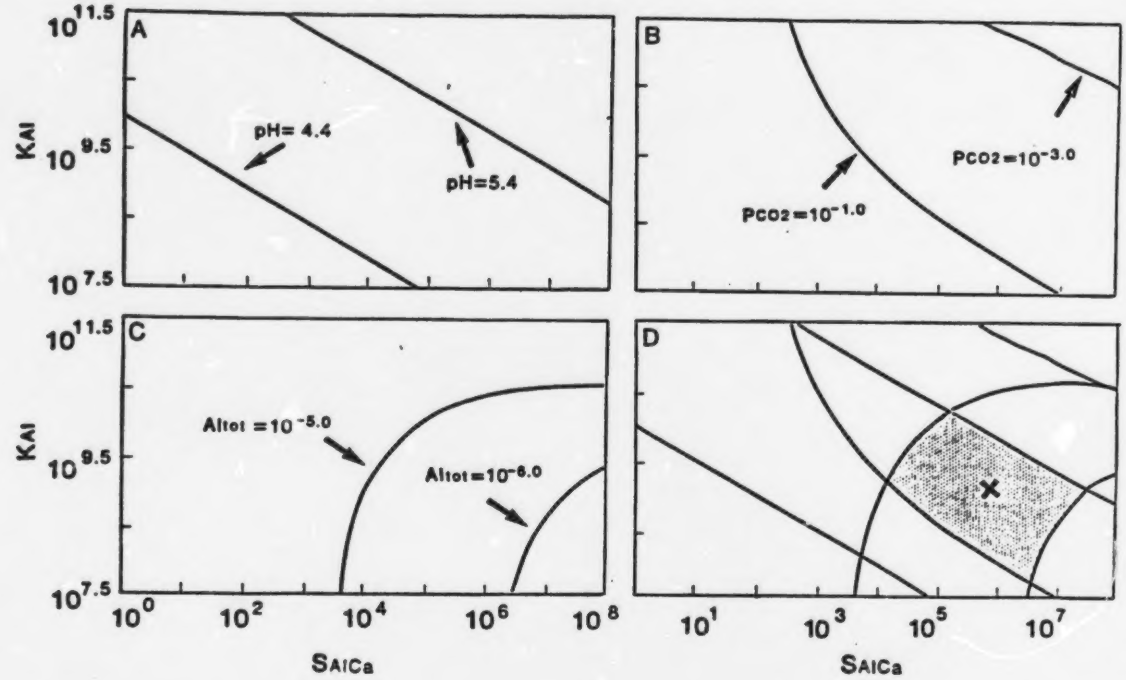

Figure A.4.10. Model response surfaces for predicted values of A) pH, B) pCO_2 and C) (Al_{tot}) as functions of the parameters K_{Al} and S_{AlCa} ($S_{CaNa} = 10^{-1.4}$, $S_{KNa} - 10^{0.32}$, $E_{Na} = .0015$). Acceptable model responses for each predicted variable lie between the solid lines in the appropriate figure. The shaded area in D represents the intersection of the response surfaces in A-C. Values of K_{Al} and S_{AlCa} which fall within the shaded region in D will produce acceptable model predictions for all three soil properties simultaneously. The x designates the values chosen for K_{Al} and S_{AlCa}.

Table A.4.6. A) Ranges, selected for the parameters required by the model, and B) ranges chosen for the responses by which the model is tested. Also shown are the parameter values chosen as a result of the regionalized sensitivity analysis (RSA).

A Parameter or variable	Observed at WOR min.	Observed at WOR max.	Ranges Used for RSA min.	Ranges Used for RSA max.	Final parameter values
S_{CaNa}	$10^{-2.6}$	$10^{0.37}$	$10^{-2.7}$	$10^{0.3}$	$10^{-1.4}$
S_{KNa}	$10^{-0.19}$	$10^{1.39}$	$10^{-0.5}$	$10^{1.5}$	$10^{0.32}$
S_{AlCa}	$10^{0.78}$	$10^{7.64}$	$10^{0.0}$	$10^{8.0}$	$10^{5.83}$
K_{Al}	no field data[a]		$10^{7.5}$	$10^{11.5}$	$10^{9.06}$
E_{Na}	.0002	.0021	.0002	.0022	.0015

B Model responses	Range Observed at WOR min.	Range Observed at WOR max.	Ranges of Acceptable Behavior min.	Ranges of Acceptable Behavior max.
BS	.006	.067	.007	.035
$Al_{tot,}$ mol L^{-1}	$10^{-6.15}$	$10^{-4.87}$	$10^{-6.0}$	$10^{-5.0}$
pH	3.9	6.5	4.4	5.4
P_{CO2}, atm	no field data[b]		$10^{-3.0}$	$10^{-1.0}$

---

[a] experimental values range from $10^{8.1}$ (synthetic gibbsite) to $10^{10.8}$ (amorphous gibbsite); see Table 3

[b] measurements at other sites range from $10^{-3.0}$ to $10^{-1.0}$; see text for details

Table A.4.7. Results of regionalizes sensitivity analysis of the model. A total of 300 model runs were made for the analysis. Significant sensitivities at the 0.01 level are indicated with yes.

Variable	Defined Acceptable Range	Number of Acceptable Responses	Significant Sensitivity				
			S_{CaNa}	S_{KNa}	E_{Na}	K_{Al}	S_{AlCa}
BS	.007 to .035	84	yes	yes	no	no	no
pH	4.5 to 5.4	127	yes	no	no	no	no
Al_{tot} mol L^{-1}	$10^{-6.0}$ to $10^{-5.0}$	82	yes	no	no	yes	yes
P_{CO2} atm	$10^{-3.0}$ to $10^{-1.0}$	117	yes	no	yes	no	yes

watersheds but seasonal measurements generally are not available. Depth of the permeable material is not currently available for most watersheds, inasmuch as soil survey data generally are limited to the upper 2 m. *In situ* estimates of primary weathering rates are sparse but may represent the major soil processes in the neutralization of acid deposition. For short term simulations (i.e., 3-5 years), estimates of soil CO_2 concentrations and exchangeable parameters are important contributors to model sensitivity. For long term simulations (i.e., 30 years or greater), estimates of primary model weathering rates are the greatest contributors to model sensitivity and predicted output.

4.6.5.6 Model Testing/Application

The MAGIC model has been calibrated on the White Oak Run watershed in the Shenandoah National Park in Virginia for the period 1980-1982. The calibrated model was then used to predict changes in stream chemsitry based on reconstructed acid deposition inputs from 1844 to the present (i.e., 1984) and deposition scenarios from 1984 to 2124. Limited deposition data exist for years prior to 1970. Therefore, it is not possible to evaluate the prediction results. MAGIC also has been calibrated on the Woods Lake, New York, data but results are not yet available.

Results from the MAGIC model are intuitively satisfying and conform with current thoughts on surface water acidification. The long term predictions based on a historical and future scenario of atmospheric SO_4^{2-} deposition are reasonable. MAGIC produces results that are consistent with the Galloway *et al.* (1983) qualitative model of surface water acidification. The Galloway *et al.* (1983) model served (in part), however, as a conceptual frame for the MAGIC model. Therefore, consistent results are not surprising.

There are other assumptions in this and other models (explicit and implicit) that must be included in any evaluation. In many cases, our ability to model these catchment processes is limited by a lack of field and laboratory data. Development of any model must proceed simultaneously with research and experimentation on the processes on which the model is based (Cosby *et al.*, 1984). Error propagation and prediction uncertainty are determined not only by the quality and precision of the field data used to calibrate and drive the model, but also by the uncertainty in model structure (formulations) and model parameterization. Uncertainty analyses have not been conducted on the MAGIC model but are being formulated.

4.6.5.7 Model Utility

The MAGIC model can be used to:

1. investigate the time response of delayed watersheds;
2. assist in defining potentially sensitive or susceptible systems to acid deposition;
3. evaluate the relative importance of sulfate adsorption, base supply, and other soil processes;
4. identify water quality parameters that are particularly sensitive to acid deposition;
5. discern patterns of dynamic behavior for water quality parameters that are sensitive to acid deposition (Cosby *et al.*, 1984);
6. develop integrated, process-oriented approaches to evaluating the effects of acid deposition on surface water chemistry.

4.6.6 Birkenes Model

4.6.6.1 Purpose of Development (Objectives)

During the 1970s, detailed deposition and water chemistry measurements were made in about 40 gaged catchments in Norway, as a part of the Norwegian SNSF Project. One of these catchments is found at Birkenes, about 15 km north of Kristiansand on the southern coast of Norway. Birkenes is a small (0.4 km^2) watershed about 200-300 m above sea level with granitic bedrock and thin podsolic soils, most of which are covered by coniferous forest. The hydrology of the watershed is characterized by wet (high discharge) periods during spring and fall and dry (low flow) periods during summer and winter.

Christophersen and Wright (1981) and Christophersen et al. (1982) developed a dynamic model of streamwater hydrology and chemistry for the Birkenes watershed. They chose this watershed as the basis for their study because of its small size, extremely low ability to neutralize acidic deposition, location in an area of high acidic deposition rates, and because of the extensive data base that was available. Their stated purpose for the development of the Birkenes model was "to test whether the observed (short term) variations in streamwater chemistry can be quantitatively accounted for by a small number of physically realistic processes" (Christophersen et al., 1982). Thus, their principle interest was in looking at short term (i.e., within season) variations in water chemistry, rather than long term effects such as watershed acidification or recovery.

4.6.6.2 Conceptual Basis

The Birkenes model is divided into three major submodels that deal with hydrology, sulfate, and cations, respectively. The original model only incorporated the first two submodels (Christophersen and Wright, 1981); the cation submodel was incorporated at a later date (Christophersen et al., 1982). To describe the conceptual basis of the model, we will discuss each of these submodels in turn. Details of the Birkenes model are provided in Appendix B.

4.6.6.2.1 Hydrology

The hydrology model drives the other two models, and is thus, arguably, the most important of the three. The authors of the Birkenes model emphasize the importance of having an accurate hydrological model before attempting to model the flux of chemical constituents. Their model is based on a modified version of a model developed by Lundquist (1976, 1977). The soils through which water flows are divided into two compartments, called the upper and lower reservoirs. Water entering the upper reservoir normally infiltrates downward to the lower reservoir, unless the latter is full. When this occurs, runoff originates from the upper reservoir. Such runoff is called quickflow. Quickflow water tends to have relatively little opportunity for contact with soils with high acid neutralizing capacities, and thus its quality tends to be similar to that of precipitation. Runoff from the lower reservoir is called baseflow, and is the only component of flow during dry periods, since the upper reservoir becomes dry. Baseflow tends to be "older" water (i.e., the water has been in contact with soils for longer periods of time) and is thus typically higher in base cation concentrations. Given these substantial differences between the quality of baseflow and quickflow, it is evident how important it is to be able to model accurately the relative contribution of each to runoff.

The hydrology model accounts for precipitation, evapotranspiration, infiltration to the lower reservoir, and discharge of water from both reservoirs to the stream. It does not include movements of water from the lower to the upper reservoir.

4.6.6.2.2 Sulfate

Sulfate is the only anion included in the Birkenes model. Nitrate is considered negligible as is bicarbonate, inasmuch as the streamwater has an average pH of 4.5. Chloride concentrations are significant, but appear to be closely associated with sodium. Both sodium and chloride have been excluded on the basis of the assumption that they balance each other perfectly, and do not influence the concentrations of other ions.

Sulfate enters the system as wet and dry deposition of SO_4^{2-} and SO_2. Once it enters the upper reservoir it is subject to adsorption/desorption processes, which are represented by a linear equilibrium model. As well, when the upper reservoir is dry, sulfate mineralization occurs. This results in elevated sulfate levels (over what would be expected from deposition rates alone) in the first runoff after an extended dry period.

In the lower reservoir, only adsorption and desorption are assumed to occur. In this case, sulfate concentrations approach an equilibrium value exponentially through time, with a relatively long half-time (45 days). As well, a "fast" adsorption process occurs, which ensures that sulfate concentrations do not change as a result of evapotranspiration.

4.6.6.2.3 Cations

The only cations included in the model are calcium, magnesium, aluminum, and hydrogen. Sodium is excluded along with chloride (see above). Potassium and ammonium are considered negligible. Calcium and magnesium are assumed to be sufficiently similar in nature to be lumped into a single parameter.

The cation submodel is based on three primary constraints. First, electroneutrality requires that the total concentration (in equivalents) of all cations must equal that of sulfate. Second, the relative concentrations of hydrogen and aluminum are determined by the gibbsite solubility equation. Third, the ratio of hydrogen ion concentration to base cation concentration is a constant, which implies a constant lime potential.

In the upper reservoir, base cation concentrations are determined primarily by ion exchange (third constraint above), whereas in the lower reservoir, weathering also replaces hydrogen ions with base cations; also some base cations are adsorbed along with sulfate (to preserve charge balance). When the upper reservoir is dry, the pool of water-soluble base cations is increased incrementally, to account for the observed relatively high base cation to hydrogen ratios in the first runoff following a dry period. Ion exchange (upper reservoir), weathering and adsorption/desorption (lower reservoir) also influence hydrogen ion concentrations. Gibbsite dissolution occurs in both reservoirs, and obviously influences both aluminum and hydrogen. Finally, aluminum adsorption/desorption can also occur in the lower reservoir.

4.6.6.2.4 Model Resolution

As mentioned earlier, the model is divided vertically into two compartments, or reservoirs, with fluxes of both water and chemical constituents occurring from the upper to the lower compartment. Also implicitly represented are (1) an atmospheric compartment, from which the inputs of water and sulfate derive; and (2) a runoff compartment, into which soil water is discharged. The model either implicitly assumes that the watershed is homogeneous, or that the estimated parameter values represent the average conditions, which are reflected in the observed runoff characteristics. The model runs on a daily time step, and only considers the snow free seasons of the year.

4.6.6.2.5 Key Assumptions

The Birkenes model includes a number of key assumptions, some of which were identified in the discussion above. Some of the more important assumptions are the following:

1. Calcium and magnesium can be considered identical in their chemical behavior.
2. Several ions do not need to be included: Na^+, K^+, NH_4^+, NO_3^-, Cl^-, HCO_3^-.
3. Organic ion concentrations are constant and unimportant.
4. The amount of organically complexed aluminum is constant.
5. All chemical reactions except weathering and adsorption/desorption in the lower reservoir reach equilibrium on a daily time scale.

4.6.6.3 Model Inputs

The primary inputs that drive the model are daily measurements of precipitation volume, air temperature, and atmospheric SO_4^{2-} and SO_2 concentrations. As well, the model requires estimates of a number of initial conditions and parameters to define the hydrological and chemical processes that are simulated. These input requirements are summarized in Table A.4.8.

4.6.6.4 Model Outputs

The outputs of the model are daily runoff rates and concentrations of each of the chemical constituents included in the runoff. The performance of the model is evaluated not only by comparing these daily outputs with observation, but also by computing total seasonal discharge and seasonal outputs of each of the ions. In the publications describing the model, the authors present the results graphically, showing plots of changes in discharge and ion concentrations throughout the snow free season.

Table A.4.8. List of Input Requirements for the Birkenes Model

---

Inputs:

- daily precipitation volume
- daily SO_4 and SO_2 concentrations
- daily mean air temperature

Initial Values:

- water amounts in each reserovir
- water soluble sulfate on solid phase in upper reservoir
- sulfate concentration in lower reservoir

Parameters:

- watershed elevation and latitude
- dry deposition velocities for SO_4, SO_2
- hydrological parameters:
  - maximum storage for upper reservoir
  - maximum and minimum storage for lower reservoir
  - routing (infiltration) parameter
  - reservoir drainage half-times
- SO_4 mineralization rate (upper reservoir)
- cation production rate during dry periods (upper reservoir)
- SO_4 adsorption/desorption equilibrium constant (upper reservoir)
- SO_4 adsorption/desorption equilibrium concentration and half-time to equilibrium (lower reservoir)
- gibbsite solubility product
- lime potential (for cation exchange)
- weathering rate half-time (lower reservoir)

4.6.6.5 Sensitivity Analyses

The only discussion of sensitivity analyses of the Birkenes model is provided by Christophersen and Wright (1981). They discuss the sensitivity of the sulfate model to the parameters they use for adsorption/desorption in both reservoirs. They do not provide, however, any indication of their uncertainty in these parameters, so it is difficult to evaluate the significance of their findings. Generally, they did not find the performance of the model was significantly affected (at least during the snow free season) by varying the parameters over the range they chose.

The authors of the model also point out that they experimented with more complex representations of some of the processes included in the model (e.g., a non-equilibrium adsorption relationship for the upper reservoir), but invariably found no significant improvement in model predictions. They do not describe their criteria for determining whether an improvement has been achieved.

4.6.6.6 Model Testing/Application

Apparently (i.e., from available publications), the Birkenes model has been applied to three catchments; two in southern Norway and one in central Ontario. At Birkenes, the model was calibrated using three years of data (1973-75) and then tested against data from the following three years (1976-78). The hydrology submodel performed most successfully, at least when evaluated on the basis of predicted total seasonal discharge. It was still described as, overall, the weakest link of the model, however, since anomalies in daily hydrology seem to be responsible for erroneous predictions of daily chemistry. Seasonal patterns of sulfate outputs compared reasonably well with observation (spring and fall flushes of SO_4 were predicted), but the total predicted sulfate outputs were less accurate than were the aggregate discharge predictions. Aluminum was generally underestimated, but the most substantial errors were in the predictions of base cation concentrations. The model predicted much greater variations than have been observed in these concentrations between low flow and high flow periods. The authors ascribe these errors to the tendency for the hydrologic submodel to predict that flow is almost always dominated by either quickflow or baseflow, rather than a mixture of both. Finally, the model was successful in reproducing the observed inverse relationship between base cation and hydrogen ion concentrations, as well as a positive correlation of hydrogen ion with discharge.

The Birkenes model has been applied to another, nearby catchment at Storgama (Christophersen et al., 1984). The Storgama catchment is quite similar to Birkenes, but is at a higher elevation and further north, so it receives less deposition of acidic materials and experiences substantial snow accumulation in winter. To apply the model to Storgama, Christophersen et al. (1984) made a number of important modifications. First, they added a snowmelt model, so that the simulations could cover an entire year. As well as modeling snow accumulation and ablation, the snowmelt model also accounts for the chemical fractionation effect as observed by Johannesson and Henriksen (1978). Second, the authors included a sulfate reduction component for the upper reservoir to act during wet periods as the reverse of the dry period mineralization process. Third, nitrate is included in the charge balance constraint inasmuch as it appears to be important during snowmelt, but is actually modeled (i.e., observed daily concentrations are provided as inputs). Finally, they also discuss the incorporation of inorganic carbon (HCO_3 and pCO_2), although they do not actually include these constituents in the model.

The performance of the Storgama model was comparable to that for the Birkenes model. Overall patterns were reproduced fairly accurately but specific events, such as an observed decline in streamwater hydrogen concentrations during winter, were not predicted. The authors provide suggestions for modifications to the model that might improve its ability to predict these events.

More recently, the Storgama version of the model has also been applied to one of the subcatchments of Harp Lake in Ontario, Canada (E. De Grosbois, personal communication). Only the hydrology and sulfate submodels have been applied so far. Once again, the hydrology submodel appears to perform quite well (here, least squares criteria have been used to evaluate performance). Application of the sulfate submodel has been less successful.

4.6.6.7 Model Utility

As stated in the introduction to this section, the Birkenes model was developed to try to explain short term variations in streamwater chemistry. In this regard, the model has been reasonably successful, especially considering its relatively simple conceptual structure. The model is not well suited, however, for looking at long term effects of acidic deposition on surface waters. The principal reason for this limitation is that the model does not account for the depletion of base saturation (and thus changes in the lime potential) or exhaustion of the sulfate adsorption capacity of the watershed. Given that these two processes are fundamental to determining the rate at which systems will respond to acidic deposition, their combined absence from the model severely limits its utility as a method for classifying the long term response characteristics of systems.

In their discussion of the Storgama version of the model, Christophersen et al. (1984) consider approaches to looking at long term questions. Inasmuch as both Storgama and Birkenes already have acidic surface waters, their interest was in looking at the long term effects of reductions in deposition rates. They consider the incorporation of inorganic carbon into the model and develop a series of theoretical relationships among anion inputs and cation (H^+ and Ca + Mg) outputs, based on various assumptions about model parameters. They themselves point out, however, that these relationships do not account for changes in lime potential.

Although the Birkenes model may not be useful for assessing the long term rate at which systems respond due to base cation depletion or sulfate adsorption, it may nevertheless be useful for other questions related to response characteristics. In particular, the hydrological submodel may provide a simple basis for evaluating the hydrologic characteristics of the system that are critical to its response. The fact that the model has been applied with reasonable success to a watershed (Harp Lake) in an area far removed from its original site of development and application, suggests that its generality may be quite high. It may be quite informative to consider its applicability to other areas where sufficient data are available for its calibration and testing.

4.6.7 Integrated Lake-Watershed Acidification Study (ILWAS) Model

4.6.7.1 Purpose of Development (Objectives)

The ILWAS model was developed to further understanding of how atmospheric and terrestrial acid-base processes interact to produce observed surface water quality. In particular, emphasis was placed on being able to predict the response of surface waters to increased, decreased, or constant loadings of acidic deposition. Early work by members of the ILWAS team indicated that the response predicted must include not only pH and alkalinity but also the concentrations of aqueous aluminum species, including organically and inorganically complexed monomeric aluminum. Aluminum had to be included because of its importance to the acid-base chemistry of acidic waters and because of its toxicity to aquatic biota.

To make such predictions, the model simulates the movement of rain and snowmelt water through the terrestrial and surface water systems (Figure A.4.11), and the major processes which add acid or base to the through-flowing water. In simulating water quality, both equilibrium and rate processes are included and a total of 16 chemical compontents are followed throughout the lake-watershed system (Table A.4.9).

From its conceptualization in 1978, the ILWAS model has been developed as a dynamic rather than as a steady-state model for three important reasons:

1. It is necessary to be able to predict the time frame over which water quality will change in response to changes in deposition acidity.
2. Critical acidity conditions can be episodic (e.g., spring snowmelt).
3. Because of the relative constancy in atmospheric acidity loads, the best test of a lake-acidification model to its ability to predict seasonal and episodic variations in surface water quality. Predicting average concentrations may mask critical conditions and is less of a test of a model's formulation.

The major facets of the ILWAS model are summarized in Table A.4.10. Its theoretical basis, development, and application are described in detail in the following references: Gherini *et al* (1984), Chen *et al*. (1983), and Goldstein *et al*. (1984).

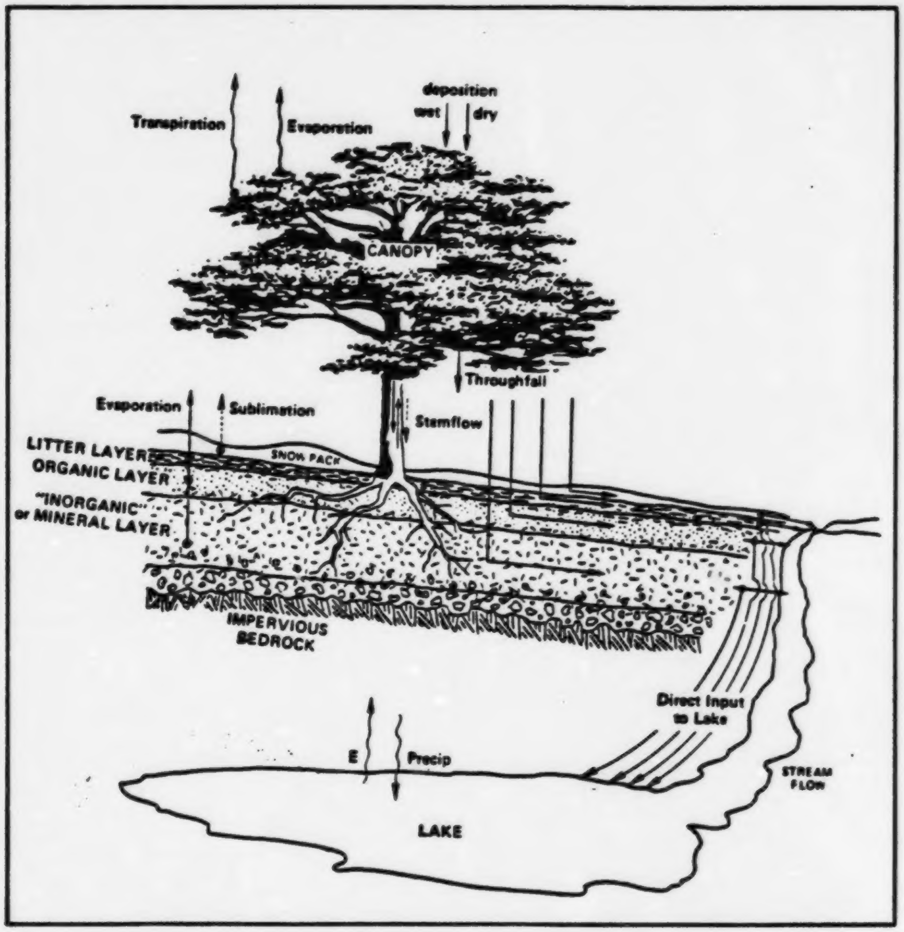

Figure A.4.11. Movement of rain and snowmelt waters through a forested lake-watershed system (Gherini et al., 1984).

Table A.4.9. Solution phase chemical constituents simulated by the ILWAS model.

SOLUTION PHASE CHEMICAL CONSTITUENTS SIMULATED BY THE ILWAS MODEL

	Cations	Neutral Anions	Neutral Species	Analytical Total	Gases (Input Only)
Species Tracked by Mass Balance	Ca^{2+}	SO_4^{2-}	H_4SiO_4	Alk ANC	(SO_x)
	Mg^{2+}	NO_3^-		Org Acid 1	(NO_x)
	K^+	Cl^-		Org Acid 2	
	Na^+	$H_2PO_4^-$		Al_T	
	NH_4^+			C_T(TIC)	
				F_T	
Species Calculated from Those Above	H^+	F^-	$CO_2(aq)$		
	Al^{3+}	$Al(OH)_4^-$	AlF_3		
	$Al(OH)^{2+}$	HCO_3^-	AlR_1		
	$Al(OH)_2^+$	CO_3^{2-}	$Al(R_2)_3$		
	AlF^{2+}	R_1^{3-}	$Al(OH)_3^0$		
	AlF_2^+	HR_1^{2-}	H_3R_1		
	$Al(SO_4)^+$	$H_2R_1^-$	HR_2		
	AlR_2^{2+}	R_2^-			
	$Al(R_2)_2^+$	AlF_4^-			
		AlF_5^{2-}			
		AlF_6^{3-}			
		$Al(SO_4)_2^-$			

Table A.4.10. Summary of the ILWAS model.

- Use: Predict changes over time in surface and ground water quality given changes in precipitation acidity and air quality; test scientific hypotheses.

- Outputs: Surface and ground water flow, and the associated concentrations of 16 chemical constituents, including the base cations (Ca, Mg, K, Na, NH_4), strong acid anions (SO_4, NO_3, Cl), monomeric aluminum species, alkalinity, pH, a mono- or triprotic organic acid analogue, dissolved inorganic carbon, C_T, total fluoride, F_T, and silicic acid.

- Inputs: Basin characteristics (e.g., land slopes, soil depths, permeabilities, chemical characteristics)
  Precipitation Quantity and Quality
  Air Quality

- Code: FORTRAN 66 and FORTRAN 77
  Computer Versions: PR1ME
  IBM
  CRAY

- Lines of Code: 12,000

- Core Memory Requirement: 0.96 Megabyte

- Computer Execution Time (8 Subcatchment System - relatively detailed system)

1 year simulation:	CRAY-1A	0.5	minutes
	IBM 3081	5	minutes
	PR1ME 550	130	minutes

The Sections which follow will briefly discuss the major points of the model.

4.6.7.2 Conceptual Basis

The conceptual basis for the ILWAS model is quite simple. For water tributary to a lake or stream, the model must determine the flow pathways, the relative distribution of precipitation among the pathways, and the time spent by water traversing the pathways. In addition, the model must determine the amount of acid or base added to the through-flowing water by major watershed and surface water biogeochemical processes. Within the model, flow routing is treated by a hydrologic module; the acid-base processes, by a chemical module. The processes simulated by these two modules are discussed briefly below.

4.6.7.2.1 Key Processes and Levels of Parsimony

4.6.7.2.1.1 Hydrologic Module

The chemical characteristics of water depends upon where the water has been (Figure A.4.12). In routing the incident precipitation, the ILWAS model uses equation which determine:

1. the fraction of incoming precipitation which is rain or snow,
2. interception of precipitation by vegetation,
3. evapotranspiration,
4. snowpack accumulation and melting,
5. flow through soil layers,
6. stream flow,
7. the thermal profile of the lake,
8. the vertical distribution of lake inflow and withdrawal of outflow, and
9. lake volumetric discharge.

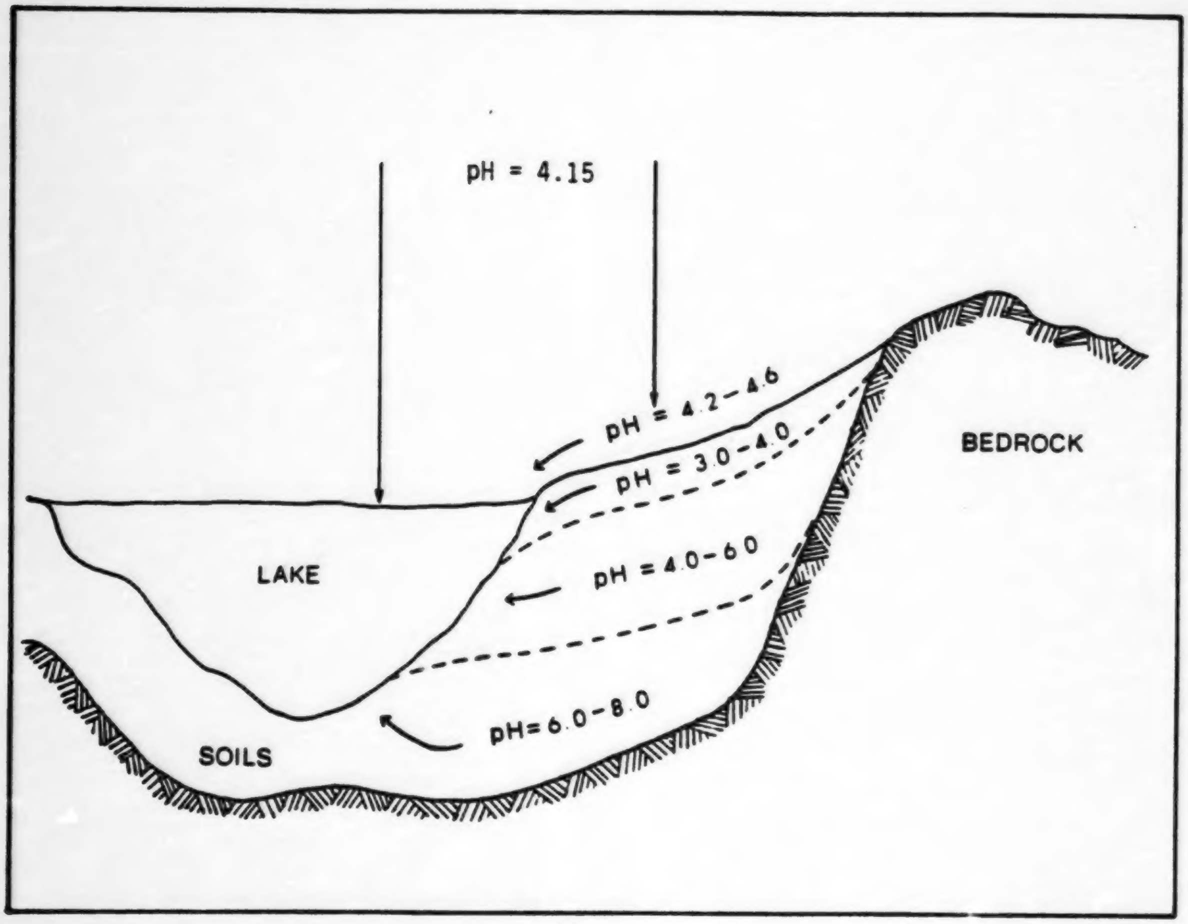

Figure A.4.12. The depth to which precipitation seeps into the soil before flowing laterally influences lake water pH (Gherini et al., 1984).

Three general types of equations are used. The mass conservation principle is used to make water balances for the snowpack, soil layers, stream segments, and lake layers. Rate equations are used to relate water flow to potential driving forces. For example, Darcy's Law is used to relate percolation and lateral flow in a soil layer to the local hydraulic processes such as evapotranspiration.

4.6.7.2.1.2 Chemical Module

The chemical module simulates those major processes that produce or consume alkalinity and a limited number of ancillary processes. In most natural waters, the carbonate system (in particular, bicarbonate) makes up over 95 percent of the alkalinity. In dilute surface waters susceptible to acidification, however, other solutes can be (and often are) important components of the alkalinity. Included are organic acid ligands and the aqueous aluminum system. To properly simulate low alkalinity waters, the ILWAS model's alkalinity definition includes these other species. The resulting extended alkalinity is defined relative to a proton reference level which includes CO_2 (aq), Al^{3+}, and H_3R_1 or HR_2 -- the latter two species being the full protonated organic acid analogues. This extended alkalinity has been shown to be mathematically (Gherini, 1984) and empirically (Schofield, 1982, 1984) equal to the Gran titration lakalinity. It can be represented by either the sum of proton acceptors minus the proton donors relative to the above proton reference level, or as the difference between the sum of the base cations* (C_B, ueq/l) minus the sum of the strong acid anions (C_A, ueq/l), (i.e., Alk = $C_B - C_A$). The use of the latter concept makes it easy to determine whether a process will acidify or alkalize a water. For example, if the process removes base cations from solution in excess of strong acid anions, it will acidify the solution.

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* Actually, the sum of the nonhydrogen cations that have charge at the equivalence point.

In the ILWAS model, the H^+-ion concentration is determined implicitly from the alkalinity and the analytical sums of total inorganic carbon, C_T (all of which are traced by the model using direct mass balance procedures).

The ILWAS model accounts for acid-base production and consumption by stoichiometric equations that quantify the amount of alkalinity produced or consumed by each reaction simulated. For example, the weathering of plagioclase, as occurs in the Adirondacks, consumes 1.19 equivalents of H^+-ion and releases an equal number of equivalents of base cations to solution for every mole of plagioclase weathered to kaolinite:

$$\overset{\text{(Plagioclase)}}{Fe(II)_{0.01}K_{0.01}Na_{0.84}Ca_{0.17}Al_{1.17}Si_{2.82}O_8} + 1.19\ H^+ + 0.575\ H_2O$$

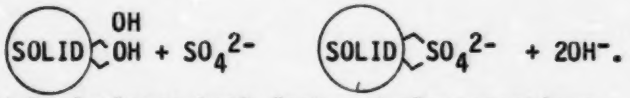
$$+ 0.0025\ O_2 \longrightarrow 0.005\ Fe_2O_3 + 0.01\ K^+ + 0.84\ Na^+ - 0.17\ Ca^{2+}$$

$$+ 1.65\ SiO_2 + 0.585\ \underset{\text{(Kaolinite)}}{H_4Al_2Si_2O_9}$$

Likewise ion exchange can replace H^+-ions with base cations, e.g.,

$$\text{SOLID}\langle Ca^{2+} + 2H^+ \qquad \text{SOLID}\langle^{H}_{H} + Ca^{2+},$$

and sulfate adsorption, by removing a strong acid anion from solution, increases the solution phase alkalinity:



$$\text{SOLID}\langle^{OH}_{OH} + SO_4^{2-} \qquad \text{SOLID}\langle SO_4^{2-} + 2OH^-.$$

The ILWAS model simulates both fast and slow reactions. Fast reactions are defined as those that go to 90 plus percent completion within hours. These reactions are represented by equilibrium expressions and reaction quotients, and include ion-exchange of solution phase acid-base equilibria. For example, the hydrolysis of Al^{3+},

$$Al3+ + H_2O \rightleftharpoons Al\ (OH)2+ + H+$$

is represented by its reaction quotient, as follows:

$$\frac{[H^+]\,[Al(OH)^{2+}]}{[Al^{3+}]} = K_{Al_1}$$

Slow reactions, on the other hand, are represented by rate expressions. For example, the weathering of plagioclase, as shown above, is slow and is represented by a rate expression of the form

$$R = \frac{-dM}{dt} = kM\,[H^+]^a$$

Where $\frac{-dM}{dt}$ = rate of decrease in plagioclase concentration

k = specific reaction rate constant

M = mass of plagioclase

$[H^+]$ = the hydrogen ion concentration

a = the power dependency of the reaction rate on the concentration of hydrogen ion.

Other rate expressions used include saturation kinetics (e.g., for nitrification) and mass-action-limited approaches to equilibrium (e.g., for the dissolution of gibbsite).

Chemical processes simulated by the model are presented in Table A.4.11. Canopy processes are simulated to include the enhanced capture of dry deposition which occurs on leaf surfaces. Tree growth is simulated, in part, because nitrient uptake can produce acidity in comparable amounts to atmospheric deposition. Quantitatively many of the most important acid-base processes occur in the soils. A schematic of these processes, occurring within a single soil layer, is shown in Figure A.4.13.

Table A.4.11. Chemical process simulated by the ILWAS model.

CHEMICAL PROCESS SIMULATED BY THE ILWAS MODEL

Canopy Processes

Dry Deposition
Foliar Exudation
Nitrification
Solution Phase Equilibration

Snowpack Processes

Accumulation
Sublimation
Leaching

Soil Processes

Litter Accumulation
Litter Decay
Nitrification
Nutrient Uptake (tree growth)
Root Respiration
CO_2 Exchange
Competitive Cation Exchange (Ca, Mg, K, Na, NH_4, H)
Anion Adsorption (SO_4^{2-}, PO_4, organic acid)
Mineral Weathering (up to 5 minerals)
Aluminum Dissolution - Precipitation
Solid-Liquid-Gas Phase Equilibration

Surface Water Processes

Gas Transfer
Mixing (Advection & Dispersion)
Heat Exchange
Algal Nutrient Uptake
Nitrification
Reductive Loss of Strong Acid Anions
Solution Phase Equilibration

4.6.7.2.1.3 Resolution

4.6.7.2.1.3.1 Temporal Resolution

The ILWAS model time step is set by the model user. Because of the solution techniques used by the model, short time steps are not necessary for either model stability or for convergence -- any time step can be used. Typically, daily time steps have been selected by model users. This gives good temporal resolution and still allows long-term (> 50 years) simulation runs to be made at reasonable cost. Much of the input data used by the monthly precipitation quality. Model output can be made on a daily, weekly, or annual basis, at the model users discretion. Typically, predicted flows and concentrations are plotted daily and elemental cycle charts are produced yearly.

4.6.7.2.1.3.2 Spatial Resolution

The spatial heterogeneity in lake-watershed systems is represented in the ILWAS model by a series of interconnected homogeneous compartments. To accommodate lake-watershed heterogeneity, the hydrologic basin is divided into subcatchments, stream segments, and a lake (or series of interconnected streams and lakes) (Figure A.4.14). In each subcatchment, there are compartments to represent the canopy, snowpack and soil layers. The lake is divided into horizontally mixed layers to allow for calculation of temperature and water quality profiles.

The number of subcatchments into which the tributary watershed is divided is determined by the model user, as is the number of soil layers in each subcatchment and the number of layers in the lake. Rarely would a watershed be divided into more than about 8-10 subcatchments, a soil into more than five layers, or a lake into more than about 10 layers. A disaggregation of a forest soil into layers is shown in Figure A.4.15. An alternate layering scheme might

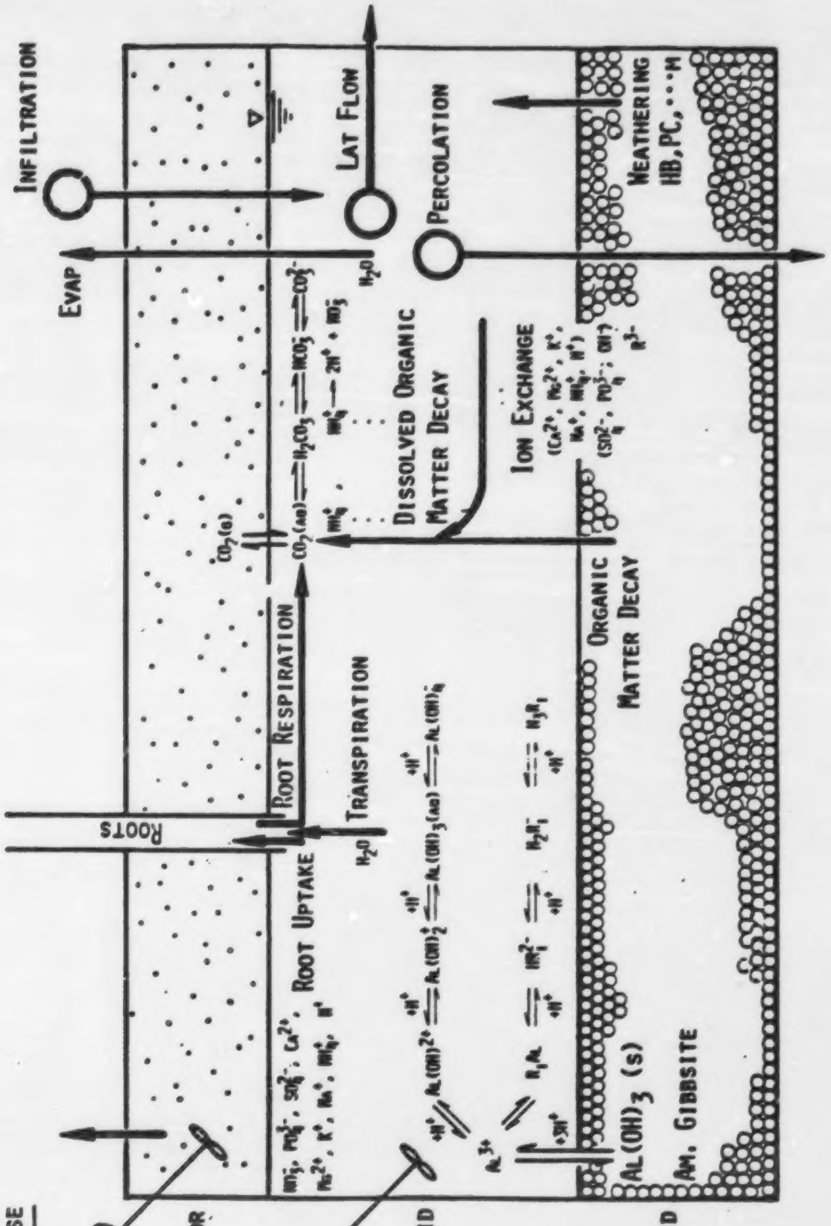


Figure A.4.13. Idealized soil layer showing major physical-chemical processes simulated by the ILWAS model (Gherini *et al*., 1984).

WOODS LAKE

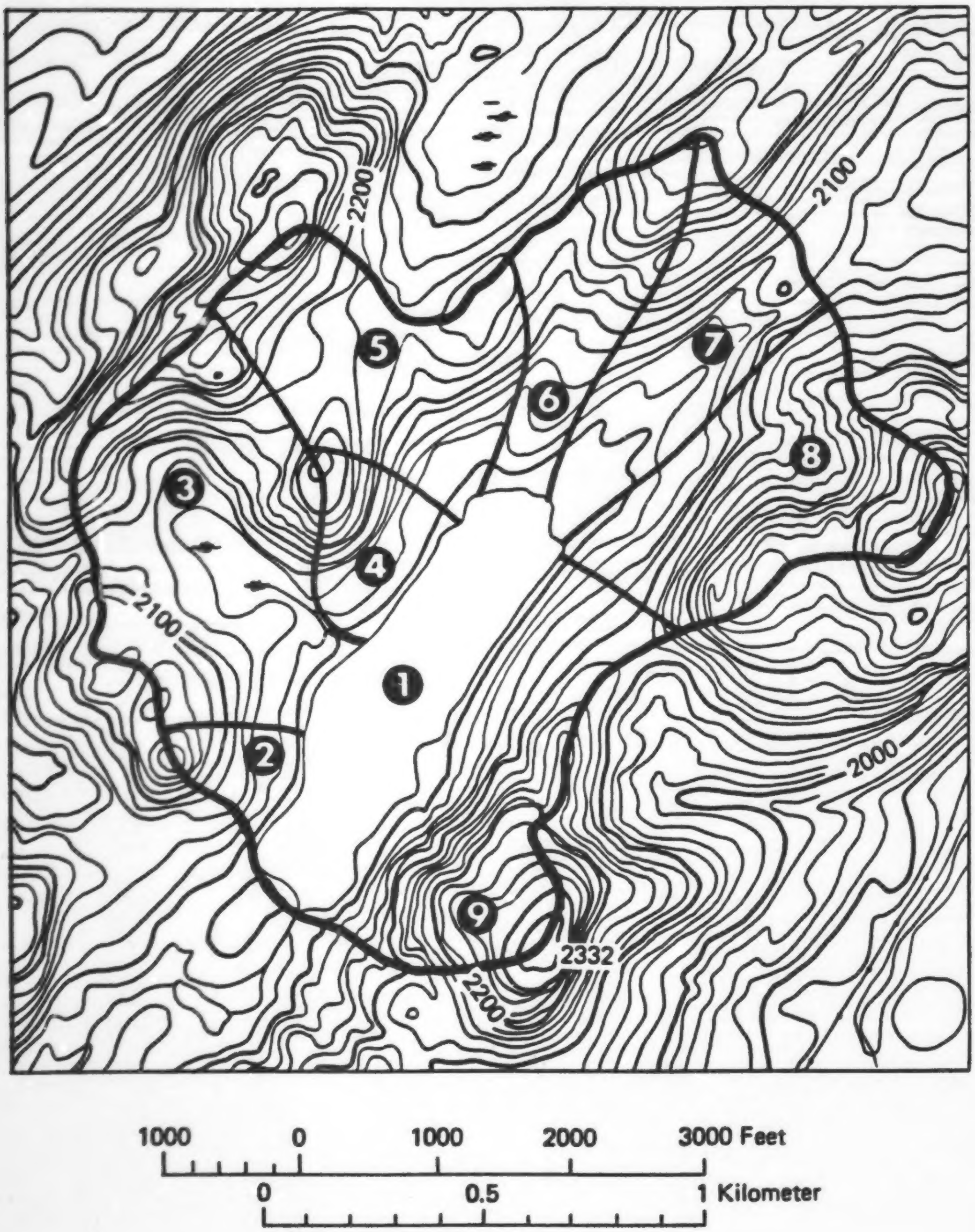


Figure A.4.14. Dividing a hydrologic basin into subcatchments and a lake (woods-lake-watershed).

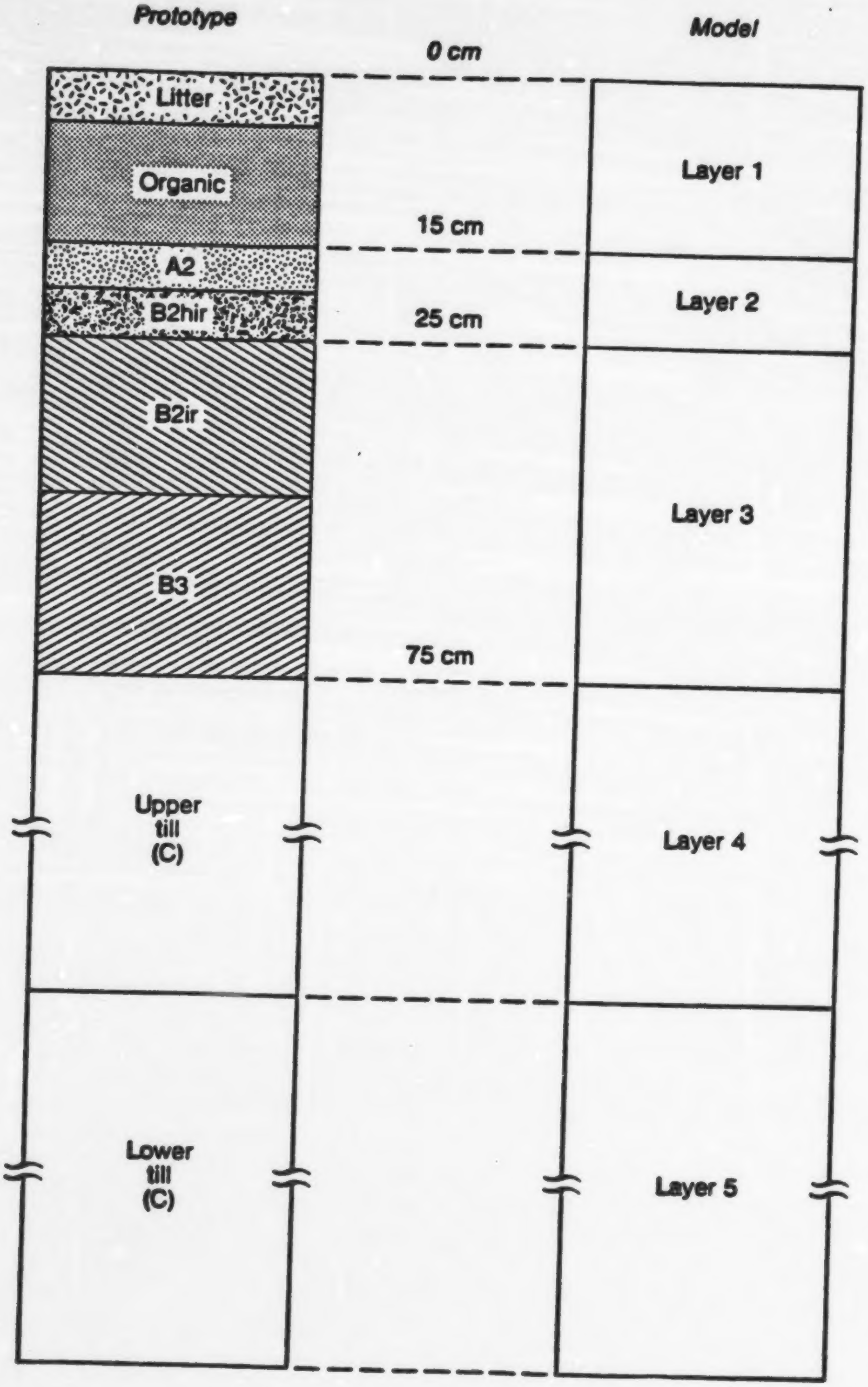


Figure A.4.15. Sample model representation of a spodic forest soil.

distinguish an organic horizon, an upper mineral horizon (A2, B2hir, B2ir, plus B3 horizons), and a deeper mineral horizon (C horizon).

4.6.7.2.1.3.3 Solution Technique

The ILWAS model represents the system modeled (apart from the lake) as a series of CSTR's as shown in Figure A.4.16. For each CSTR, for each time step, the dequence of computaitons is as shown in Figure A.4.17. The lake itself is modeled by a series of differential equations which are solved simultaneously for each of the lake layers.

4.6.7.3. Model Inputs

Inputs to the ILWAS model are of two types: time variant meteorological, air quality and precipitation data which are used to drive the model, and time invariant data which describe the hydrological and chemical properties of the basin being modeled.

The major time variant inputs required by the model are summarized in Table A.4.12. The time invariant hydrological and chemical data required are briefly described in Tables A.4.13 and A.4.14. Thermodynamic data used by the model are given in Table A.4.15. Detailed discussion of model input data is given by Gherini et al. (1984) and Goldstein et al. (1984) (see also Appendix A-2). Minimum input data requirements for the ILWAS model are listed in Table A.4.16.

Experience has shown that the parameters that are most important for calibration of the ILWAS model are the following:

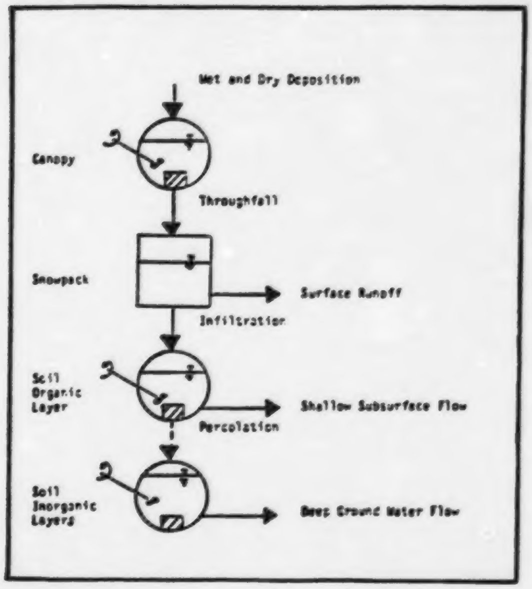


Figure A.4.16. Idealization of system compartments as CSTR's along flowpaths through a subcatchment (Chen et al., 1983).

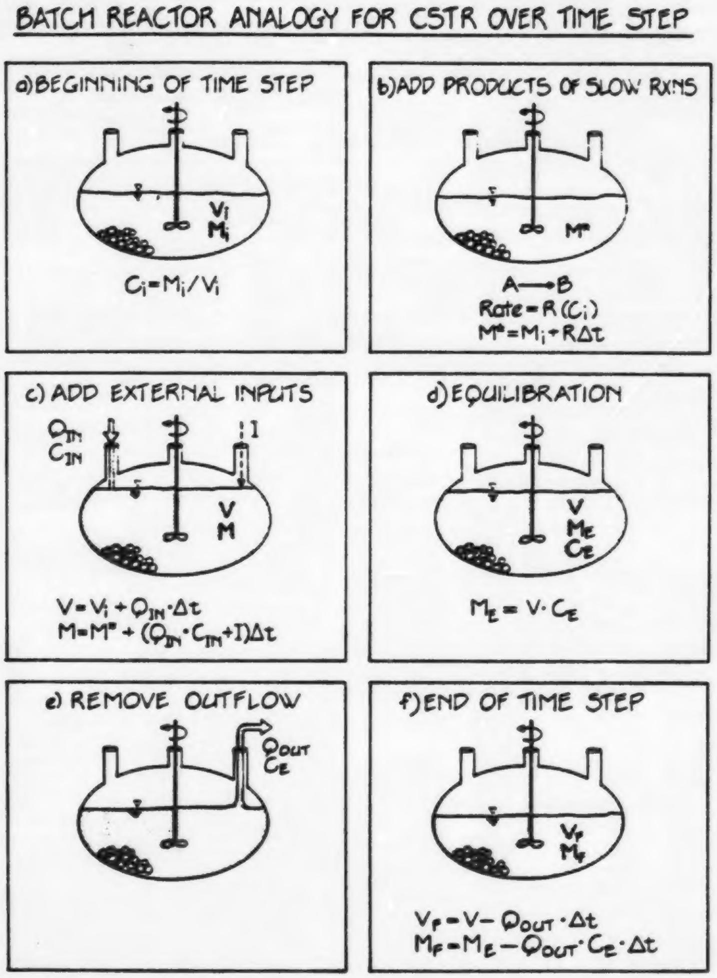


Figure A.4.17. Batch reactor analogy for single CSTR over time step (Gherini *et al.*, 1984).

Table A.4.12. Time variant model input data.

Daily precipitation
Daily minimum and maximum air temperatures
Monthly or daily precipitation quality -- major cations and anions
Monthly air quality -- major cations and anions, SO_x and NO_x concentrations

Table A.4.13. Time invariant model input data: basin hydrologic characteristics.

TIME INVARIANT MODEL INPUT DATA: BASIN HYDROLOGIC CHARACTERISTICS

Evapotranspiration Data

Monthly vegetation leaf area indices*
Monthly relative humidities
Seasonal evapotranspiration coefficients

Snowpack Data

Snow sublimation rate coefficient
Snowmelt rate coefficient
Moisture capacity of snowpack

Subcatchment Data

- Land slope
- Aspect
- Percent vegetative cover*
- Number of soil layers, and by soil layer modeled,
  - Soil layer thickness
  - Soil layer permeability
  - Soil layer field capacity
  - Soil layer saturated moisture content

Stream Data

Stream segment dimensions

Lake Data

Lake bathymetry
Depth-volume relationship
Stage-outflow relationship
Energy budget coefficients

---

* = by vegetation type (deciduous, coniferous, open area)

Table A.4.14. Time invariant model input data: basin chemical characteristics.

TIME INVARIANT MODEL INPUT DATA: BASIN CHEMICAL CHARACTERISTICS

Vegetation Data

- Monthly vegetation growth coefficients*
- Canopy and bole composition, by element*
- Monthly vegetation respiration rates*
- Monthly foliar exudation rates*
- Monthly litterfall rates*
- Gaseous and particulate deposition velocities

Soil Data

- Litter decomposition rate coefficients
- Soil nitrification rate coefficient
- Mineral weathering stoicheometries
- Mineral weathering rate coefficients
- Soil layer mineral composition**
- Cation exchange capacity**
- Cation exchange selectivity coefficients**
- Anion adsorption coefficients**
- Initial soil solution and adsorbed phase concentrations**

Surface Water

- Monthly primary productivities
- Behavior with respect to amorphous gibbsite
- Initial solute concentrations, by ion

---

* = by vegetation type (deciduous, coniferous, open area)

** = by each soil layer

Table A.4.15. Thermodynamic data used by ILWAS model.

THERMODYNAMIC DATA USED BY THE ILWAS MODEL

Ion Product of Water	: K_W	: pK_W	$= \frac{+4470.99}{T} - 6.0875 + 0.01706 \cdot T$	(Stumm, 1981, p. 127)
First Dissociation for $H_2CO_3^*$	: K_{C_1}	: pK_{C_1}	$= \frac{17052}{T} + 215.21 \cdot \log T - 0.12675 \cdot T - 545.56$	(Loewenthal, 1978, p. 84)
Second Dissociation Constant for $H_2CO_3^*$	: K_{C_2}	: pK_{C_2}	$= \frac{2902.39}{T} + 0.02379 \cdot T - 6.498$	(Loewenthal, 1978, p. 84)
Henry's Law Constant, $H_2CO_3^* / P_{CO_2}$	: K_H	: pK_H	$= \frac{-2385.73}{T} + 14.0184 - 0.0152642 \cdot T$	(Stumm, 1981, p. 204)
First Dissociation Constant for Triprotic Organic Acid Analgoue	: $K_{T_{1_1}}$	: $pK_{R_{1_1}}$	= 4.0	(Gherini, Hudson, & Cronan, 1981)
Second Dissociation Constant for Triprotic Organic Acid Analogue	: $K_{R_{1_2}}$	: $pK_{R_{1_2}}$	= 6.1	(Gherini, Hudson, & Cronan, 1981)
Third Dissociation Constant for Triprotic Organic Acid Analogue	: $K_{R_{1_3}}$	: $pK_{R_{1_3}}$	= 9.25	(Gherini, Hudson, & Cronan, 1981)
Dissociation Constant for Monoprotic Organic Acid Analogue	: $K_{R_{2_1}}$	: $pK_{R_{2_1}}$	= 4.5	(Driscoll, 1982)
Aluminum System Hydrolysis Constants	: K_{Al_1}	: pK_{Al_1}	= 4.99	Values from May *et al*., 1979. *May did not find an $[Al(OH)_3^0](aq)$ specie. Thus K_{Al_3} is set so that $A(OH)_3^0$ remains below 10^{-10} M and K_{Al_4} is adusted to compesnate for this low value of K_{Al_3}.
	K_{Al_2}	: pK_{Al_2}	= 5.15	
	K_{Al_3}	: pK_{Al_3}	= 14*	
	K_{Al_4}	: pK_{Al_4}	= 94.2*	
Aluminum-Sulfate Complexation Constants	: $K_{Al_{S1}}$	: $pK_{Al_{S1}}$	= 3.21	(Driscoll, 1982)
	$K_{Al_{S2}}$	: $pK_{Al_{S2}}$	= 5.11	(Driscoll, 1982)
Aluminum-Fluoride Complexation Constants	: $K_{Al_{F1,2,3,4,5,6}}$	: pK	= 7.02, 12.76, 17.03, 19.73, 20.92, 20.87	(ibid.)
Aluminum-Triprotic Organic Acid Analogue Complexation Constant	: $K_{Al_{R1}}$	: $pK_{Al_{R1}}$	= 11.08	(Data from Cronan and Schofield)
Aluminum Monoprotic Organic Acid Analogue Complexation Constants	: $K_{Al_{R2_{1,2,3}}}$	: $pK_{Al_{R2,1,2,3}}$	= 7.81, 14.67, 20.15	(Driscoll, 1982)
Gibbsite Solubility Product (pK_{SP} = 32.6 used)	: K_{SP}	: pK_{SP}	= 31.19 = 32.64 = 33.22 = 33.88	(Amorphous Gibbsite) (Mircrocrystalline Gibbsite) (Natural Gibbsite) (Synthetic Gibbsite)

Table A.4.16. Minimum input data requirements.

- Topographic map of the hydrologic basin (USGS 7.5 min sheets)
- Descriptions of watershed vegetation
- Daily precipitation amounts (nearby weather station data adequate)
- Monthly precipitation quality -- major cations, major anions (can be obtained from NADP)
- Estimate of dry deposition quality
- Soil depth (depth of permeable media)
- Soil permeability (if data not available, value can be estimated from grain size distribution or by model calibration to stream or lake discharge)
- Soil cation exchange capacity or grain size distribution
- Soil mineralogy -- 2-3 weatherable minerals (% by weight)
- SO_4^{2-} adsorption -- isotherm coefficients
- Stream -- length and 2-3 cross-sections
- Lake bathymetry (1 or 2 transects)
- Initial soil solution -- major cations, major anions, pH
- Initial surface water -- major cations, major anions, pH SiO_2

Hydrologic Parameters	Chemical Parameters
Land slope	Soil cation exchange capacity
Soil permeability	Soil cation selectivity coefficients
Soil depth	Soil anion adsorption coefficients
Soil field capacity*	Mineral weathering rate coefficients
Soil saturated moisture capacity*	Soil nitrification rate coefficient
Seasonal evapotranspiration coefficients*	Initial soil and surface water solute concentrations*

---

* Indicates parameters of secondary importance.

4.6.7.4 Model Outputs

Output from the ILWAS model can be produced in three major forms:

1. Plots of volumetric flow rates (e.g., lake or stream discharge) and solution chemical concentrations at various locations within the basin (lake surface water soil, soil layers, etc.) on a daily, weekly, or yearly basis;
2. cycle charts for the individual chemical constituents, which show the storage, change in storage, reaction, and fluxes between the various compartments within the basin;
3. summary tables which present the solution phase and adsorbed solute concentrations, and moisture concewntrations throughout the basin. An example of a cycle chart is shown in Figure A.4.18 for calcium, a predicted and observed lake outflow plot is shown in Figure A.4.19, and a predicted and observed pH and alkalinity plot is shown in Figure A.4.20.

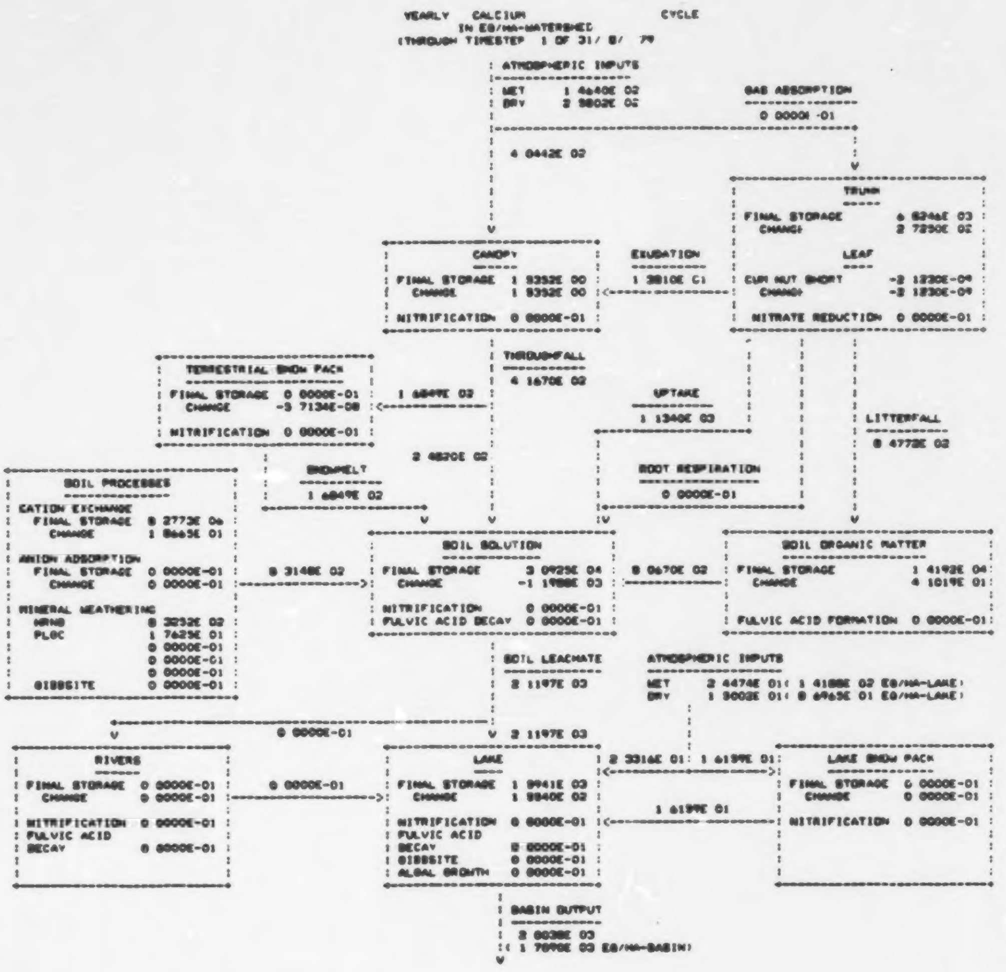


Figure A.4.18. Example yearly cycle chart for calcium (Chen et al., 1983).

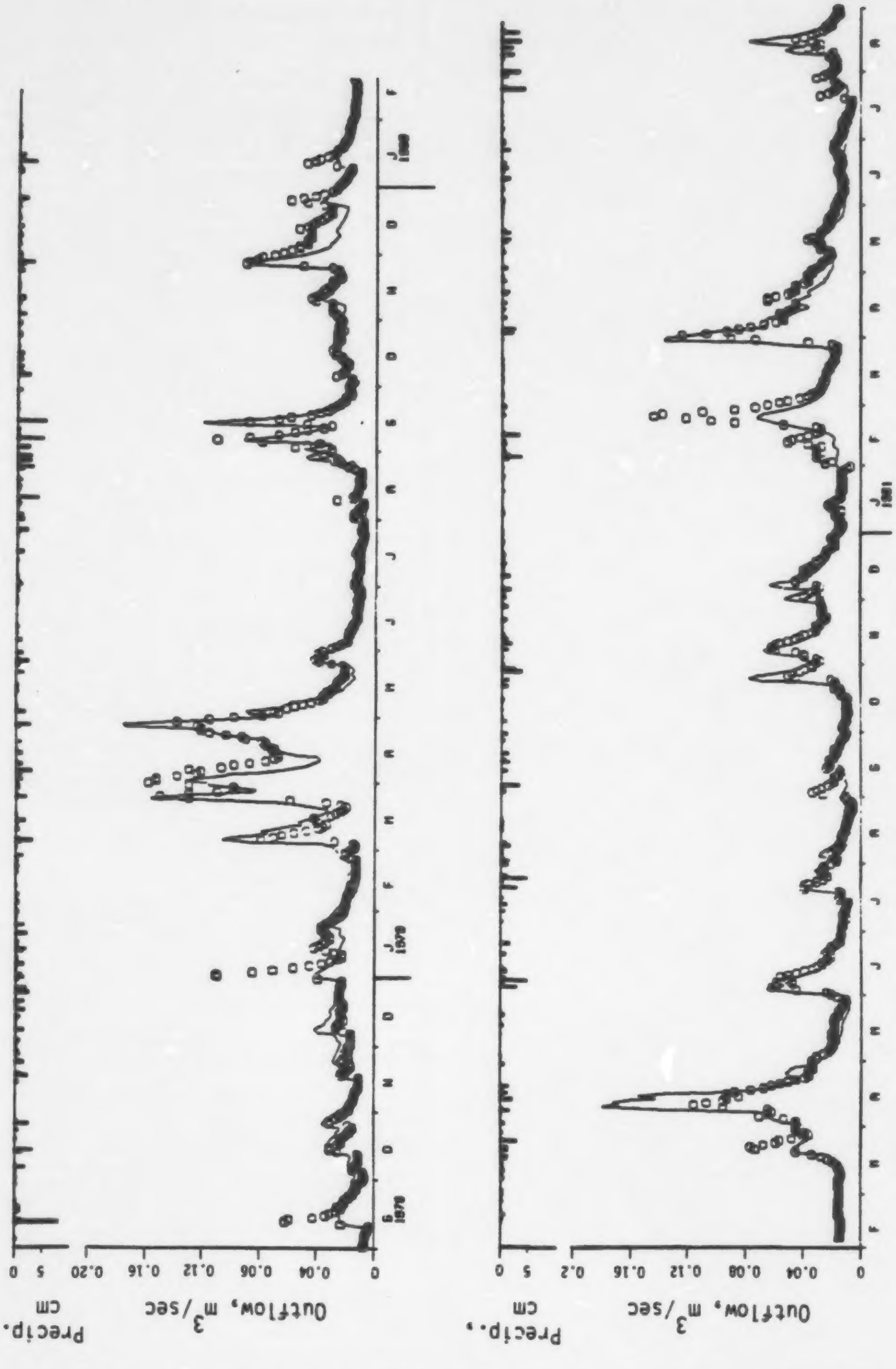
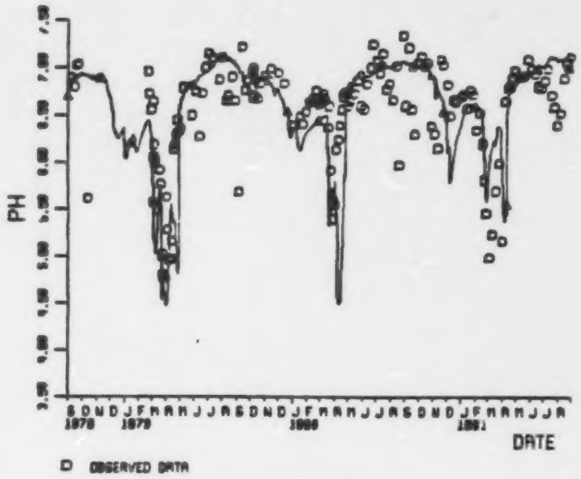
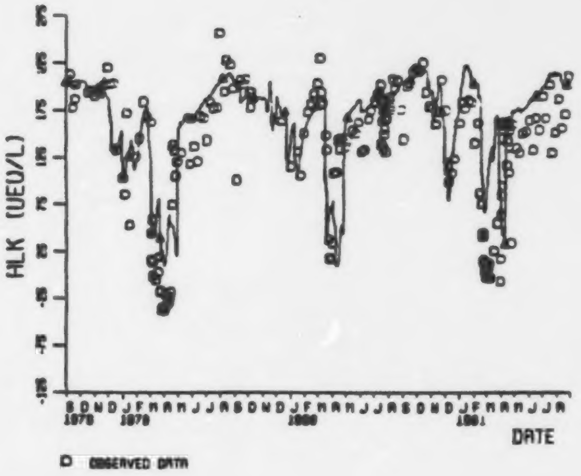


Figure A.4.19. Simulated and observed instantaneous outflow for Panther Lake. Observed values are represented by small boxes, (Gherini *et al*., 1984).



a) Panther Lake Outlet pH



b) Panther Lake Outlet Alkalinity

Figure A.4.20. Simulated and observed outflow water quality for Panther Lake: (a) pH; (b) alkalinity.

4.6.7.5 Sensitivity Analyses

Several sensitivity analyses have been performed with the ILWAS model to determine the key factors that control the volumetric discharge rates and lake water quality in systems with moderate relief (e.g., Woods and Panther basins). The hydrologic output variables and model coefficients to which these were found to be most sensitive are given below:

- Total annual lake outflow--evapotranspiration coefficient.
- Snowmelt hydrograph, rising limb--incipient snowmelt temperature.
- Snowmelt hydrograph, falling limb--snowmelt rate coefficient.
- Peak flow at lake outlet--hydraulic conductivity and thickness of organic soil horizon.
- Base flow at lake outlet--hydraulic conductivity and thickness of inorganic soil horizons.
- Non-snowmelt hydrographic recession--the difference between soil field capacity and saturation moisture content.

Factors to which lake water quality showed highest sensitivities included:

- the particle and gas deposition velocities;
- the percent litter content in the organic soil horizon;
- the soil cation exchange capacities (at low values) and the base saturation indices; and
- the rate coefficients that describe net tree productivity, litter decay, humus decay, soil nitrification, gibbsite solubilization, and mineral weathering. To display sensitivity to such parameters, the parameter values are adjusted up and down individually from the calibrated values and the responses in the lake water quality are plotted.

When such analyses are made, many of the responses are found to be nearly linear. Figure A.4.21 presents such a plot for the atmospheric particulate

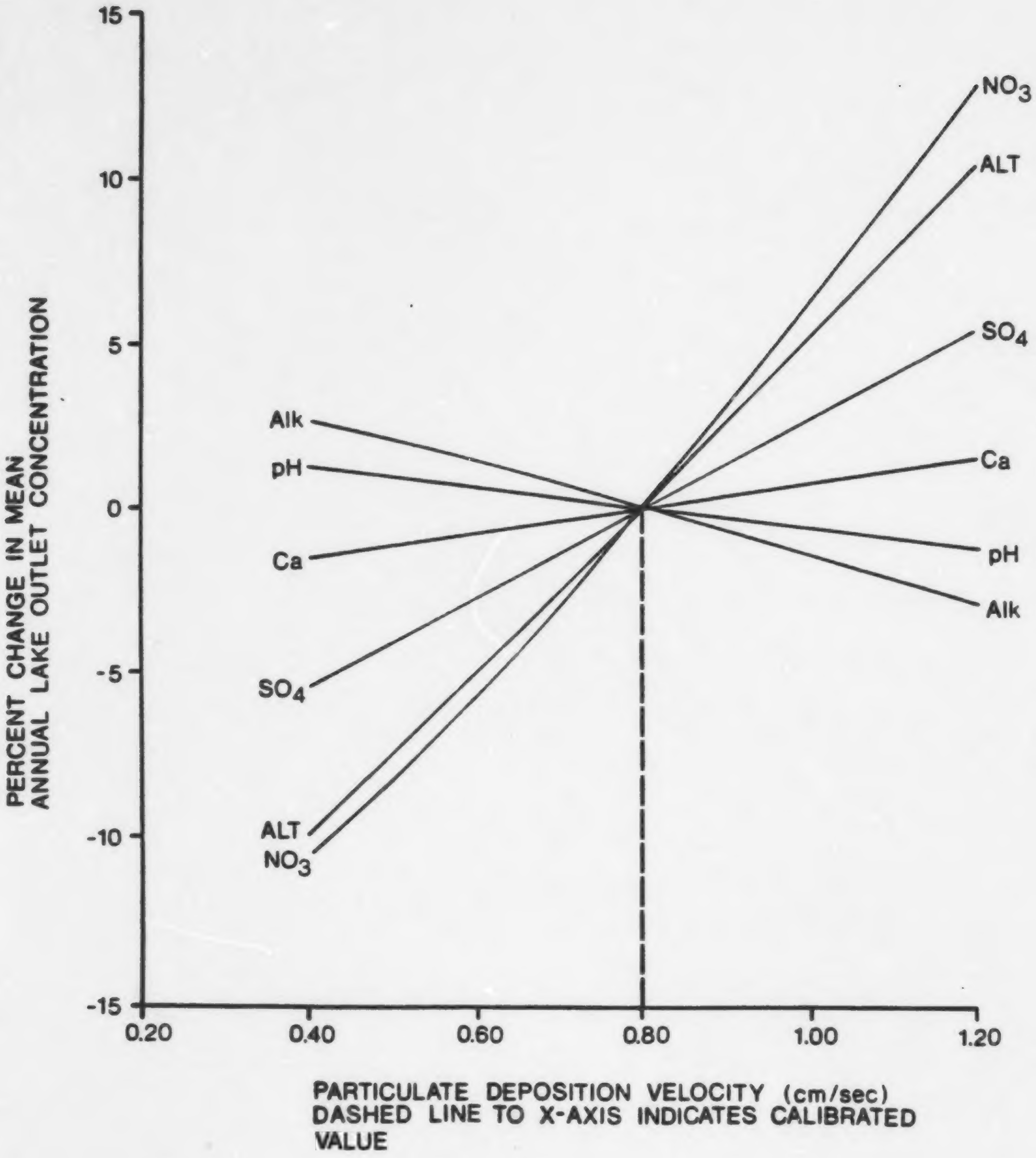


Figure A.4.21. Change in mean annual lake concentrations versus particulate deposition velocity. Second year after change in deposition velocity. Panther Lake-Watershed.

matter deposition velocity (this influences the dry depositional loading). Figure A.4.22 presents a similar plot for the soil nitrification rate coefficient. Here, some of the responses appear to be nonlinear. As might be expected, the relative sensitivities to the model parameters are site-specific. What is sensitive in Woods Lake, for example, may not be as sensitive in Panther Lake and vice versa. In general, the depositional parameters and decay rate coefficients are sensitive parameters. The cation exchange capacity and the mineral weathering rate coefficients, at the values encountered, were relatively insensitive.

4.6.7.6 Model Testing and Application

The ILWAS model was originally developed for Woods, Panther, and Sagamore Lakes in the Adirondack Mountains of New York. The same model was calibrated to all three lakes with three years of field data which included daily precipitation quantity, weekly or monthly averaged precipitation quality, weekly dry deposition measurements, daily maximum and minimum ambient air temperatures, three snowpack transect surveys per year, daily lake outlet flows, weekly water quality at the lake outlets, and monthly lake water quality profiles. Comparisons between the calculated and the observed time series of data were made at many check points within the lake-watershed system in addition ot the lake outlets. The confirmations were good and the results have been published.

After calibration, the model was used to project the lake responses to reduced atmospheric sulfate loadings. The results showed the responses to be site-specific. Panther Lake pH responded very little to a halving in the sulfate load, whereas in Woods Lake, the summertime pH increased, with the pH during the springmelt period increasing to a lesser degree (Gherini *et al.*,

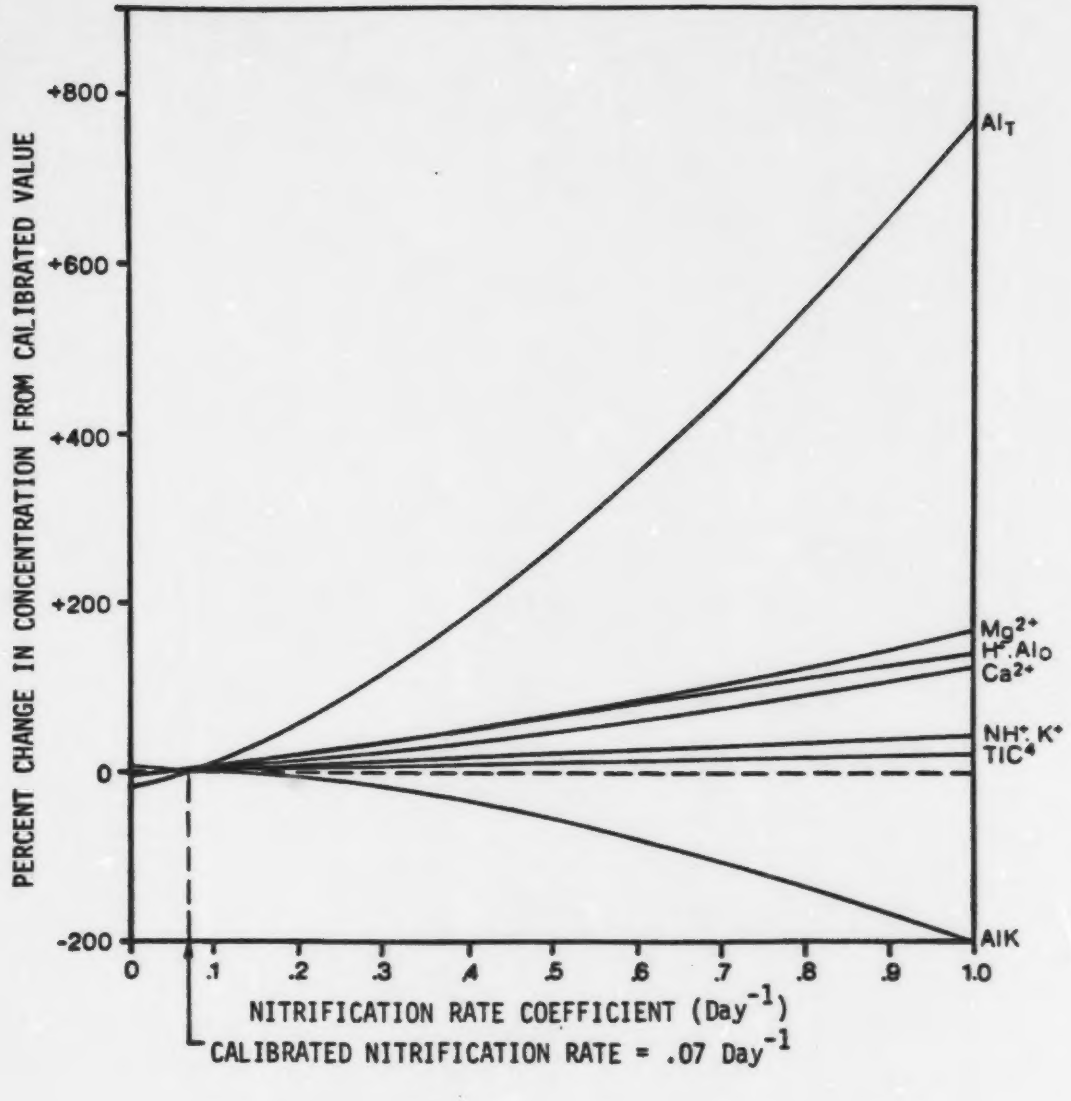


Figure A.4.22. Change in mean annual lake concentrations versus soil nitrification rate coefficient (one-year simulation, Panther Lake watershed).

1984). For these two systems, the majority of the response occurred within three to four years after the reduction in loads.

Since the original development of the model, it has been applied to seven additional basins in the Adirondacks, including seepage and interconnected lake-watershed systems. The data base used covered a two-year period with monthly water quality values. The model has also been applied to two seepage lakes in northern Wisconsin, i.e., Round Lake and East Eightmile Lake. This application is continuing. In addition, the ILWAS model has been applied successfully to a stream-watershed in North Carolina, and data are now being collected for application of the model to two lake-watershed systems in the Sierra Nevadas.

4.6.7.7 Model Utility

The ILWAS model has been used to organize the field research, identify critical knowledge gaps, and integrate project results on the ILWAS and RILWAS investigations. Its ability to project lake responses to changing deposition loads has been demonstrated. In addition, the model has been use to test scientific hypotheses. Three, 5-day hypothesis testing workshops were held with ILWAS principal investigators, U.S. EPA personnel, and utility scientists. The first day of each workshop was devoted to the presentation and discussion of model theory, model structure, hypothesis formulation and hypothesis testing procedures. On the second day, the workshop participants formulated hypotheses and projected results. Among the hypotheses formulated, 12 to 14 were selected for testing with the model during the following two days. On the fifth day, the participants regrouped to analyze the results.

A sampling of the hypotheses tested during the three workshops are given in Table A.4.17. One of the hypothesis tested was the importance of the depth

Table A.4.17. Samples of the hypotheses tested using the ILWAS model at three hypothesis testing workshops.

SAMPLES OF THE HYPOTHESES TESTED USING THE ILWAS MODEL AT THREE HYPOTHESIS TESTING WORKSHOPS

ILWAS INPUT WORKSHOP

Participants: C. Chen, N. Clesceri, C. Cronan, J. Dean,
R. Finch, S. Gherini, R. Goldstein,
A. Johannes, S. Lindberg, and C. Vasudevan

Sample Hypotheses Tested:

1. Year to year fluctuations (e.g., ±$2^{\circ}C$) in climatic temperatures alone will affect lake acidity.
2. Exudation by forest foliage does not affect lake acidity.
3. Without the presence of a snowpack and its subsequent melting, there would be no spring pH depression in Panther Lake.
4. Other things being equal, a watershed with more coniferous vegetation will have a lower lake water pH.
5. The presence of organic acid ligands in throughfall will lower the throughfall pH.

ILWAS TERRESTRIAL SYSTEMS WORKSHOP

Participants: R. April, C. Chen, C. Cronan, J. Dean, R. Finch,
S. Gherini, R. Goldstein, D. Grigal, R. Newton,
N. Peters, and C. Schofield

Sample Hypotheses Tested:

1. Long term droughts produce cycles of acidification intensity. Alkalinity will increase in dry years followed by a decrease as rainfall returns to normal levels.
2. Increasing the permeability of the mineral soil layers will increase the alkalinity supply rate of a basin.
3. Increasing the partial pressure of carbon dioxide in the soil will increase lake water alkalinity.
4. Removing hornblende from the soil will decrease the basin alkalinity output and thereby the lake water alkalinity.
5. Without any cation exchange capacity in the soils, the lake waters will become more acidic.

Table A.4.17 (continued)

Table 8 (cont'd)

ILWAS AQUATIC SYSTEMS WORKSHOP

Participants: D. Bennet, C. Chen, R. Church, C. Driscoll,
R. Finch, J. Galloway, S. Gherini, R. Goldstein,
G. Hendrey, R. Kawaratani, M. Levin, L. Mok,
N. Peters, and G. Schofield

Sample Hypotheses Tested:

1. Doubling the deposition of sulfur will double the lake water sulfate concentration within five years.

2. Decreasing the annual nitrate loading by 75% will produce a large increase in lake water alkalinity.

3. Lake water pH and alkalinity will remain the same whether the sulfate in deposition is associated with calcium or hydrogen ion.

4. Lake water pH and alkalinity will decrease if the sulfate in deposition is associated with ammonium rather than hydrogen ion.

5. Direct precipitation into the lakes does not supply sufficient phosphorus to support the observed primary productivity.

6. Soil nitrification determines spring lake surface water levels of nitrate and regulates the changes in alkalinity.

7. Net primary production in Woods and Panther Lakes has only a small effect (<5-10%) on lake water alkalinity.

8. Woods Lake, limed to pH values of 5.5, 6.0, or 6.5, will return to its original pH regime within 2 to 3 years (Alternates: Lime lake in September or place lime on lake ice in February).

9. As the watershed area tributary to a given lake decreases, so will the lake water pH and alkalinity.

of the soils (permeable media) in the tributary watersheds. It was argued that if the soil depth in Panther watershed was reduced to that of Woods, the lake waters would become acidic. To complete this test, it was hypothesized that Woods Lake waters would become alkaline if its soil depth was increased to that of Panther. The test results confirmed this hypothesis (Goldstein *et al.*, 1984).

Another hypothesis advanced was that the snowmelt associated pH depression in Panther Lake (pH dropping from about 7.2 to 4.5) would not occur if the winter ambient air temperatures stayed above freezing. It was felt that without the cold air, snow would not form and precipitation during the winter would be applied uniformly over time to the soils instead of during a short, one to two week snowmelt period. It was argued this would minimize the backup of percolation into the organic horizon and hence reduce the shallow lateral flow of water through this acidic layer. When the hypothesis was tested, no significant springtime pH depression was observed in the model output. What, at that time, appeared to be an academic result was confirmed the following year in the field when little snow fell in the Adirondacks. No springtime pH depression was observed at Panther Lake or at any of the 24 RILWAS lakes (Goldstein *et al.*, 1984).

4.6.8 Others

4.6.8.1 Bobba and Lam

Bobba and Lam (1984) have recently developed a hydrological model for investigating long-term acidification effects, which they intend to link with one or more chemistry models (Lam and Bobba, 1984). Though their model does not yet include chemical interactions, its structure is appropriate for application to the question of watershed response rates.

Conceptual Basis

The model consists of mass balance calculations for snow accumulation and melting, soil moisture budgeting, runoff generation, and hydrological routing. Structurally, the model represents the watershed as a set of subbasins, each with six compartments:

1. atmospheric inputs;
2. the snowpack;
3. an upper soil reservoir (surface litter zone);
4. a lower soil reservoir (unsaturated zone, incuding the root zones of most of the perennial vegetation);
5. a groundwater reservoir; and
6. a stream.

Snowmelt calculations are based on two empirical formulations, one for rain periods and one for rain-free periods. The input data and parameters used in these equations are listed in Table A.4.18.

The model uses three basic rules of water movement:

- aerial infiltration is proportional to the volume remaining in the upper soil zone;
- outflow from any of the three reservoirs is linearly proportional to the reservoir storage;
- evapotranspiration is proportional to the product of the potential evaporation rate (required by heat balance considerations) and the reservoir storage.

Each subbasin has its own soil moisture budget and output hydrological response. The runoff values from each subbasin are combined via a transformation function (or filter) to account for inter-subbasin differences in the time of travel and magnitude of runoff.

Table A.4.18. Estimated parameters and input data requirements in the model developed by Bobba and Lam.

Estimated Parameters	Input Data Requirements
convection-condensation melt constant	precipitation*
shortwave radiation melt factor	maximum and minimum air temperature*
infiltration coefficients for three reservoirs	solar radiation*
recession constants for three reservoirs	wind speed*
potential evaporation rate	% forest cover
	mean monthly evaporation
	watershed drainage area
	watershed soil and land cover characteristics
	initial soil moisture conditions

* Daily measurements

Model Inputs and Outputs

The input data requirements of the model are summarized in Table A.4.19. Lam and Bobba (1984) point out that for the investigation of long-term effects of acidic deposition (.e., over several decades or a century), daily flows are not necessary. A few runs of the hydrological model for some representative years are probably sufficient to establish general hydrological pathways. Past weather records can be used to establish the frequency distribution of different "types" of years.

The output of the model includes daily values for overland flow, interflow, and groundwater flow.

Model Applications

No sensitivity analysis of the model has been published. The model was calibrated to 1981 data from the Turkey Lakes Watershed (near Sault Ste. Marie, Ontario) and then verified against 1982 data from five stream stations. Agreement between observed and simulated flows was very good, particularly since there was a considerable difference in snowfall between the calibration and validation years.

The model is currently being applied to the Lake Laflamme watershed (north of Quebec City) and the Mersey River in Nova Scotia.

Utility

Inasmuch as this model does not yet include chemical processes, it cannot be used to predict the rate of watershed response. The structure of the model, however, is sufficiently simple to make an appropriate hydrological submodel for the MAGIC model, which focuses almost entirely on chemical processes.

4.6.8.2 Booty and Kramer

This model was originally developed to simulate the movement of water and hydrogen ions through a forested waershed, and to assess the parameter sensitivity of model predictions (Booty and Kramer, 1984).

The overall structure of the model is illustrated by Figure A.4.22, and summarized in Table A.4.19. The most unusual feature of the model is its use of laboratory-determined acid neutralization capacity functions for each soil horizon. These functions are meant to represent the short-term capacity of soils to neutralize inputs of varying acidity. Inasmuch as base saturation and sulfate adsorption capacity are not modeled explicity, it is not clear (at least from the Booty and Kramer 1984 paper) how the model could produce a delayed response to constant levels of deposition. Also, the model only budgets hydrogen ion concentrations and alkalinity, but not sulfate or nitrate.

A partial sensitivity analysis (independent variation of single parameters) indicated that lake acidification rates were most sensitive to: (1) infiltration-percolation rates; (2) soil depth; and (3) soil horizon acid neutralization capacities.

To date, the model has only been applied to one system: Batchawanana Lake, in the Turkey Lakes watershed. It was calibrated against one year of data on streamflow and lake pH, but validation runs have not been published. On the calibration year data, the model accurately tracked streamflow and the spring pH decline, but overestimated summer pH.

In conclusion, the absence of delay mechanisms in the structure of the model and the lack of validation tests of model predictions, make it currently inappropriate for addressing the issue of watershed response times.

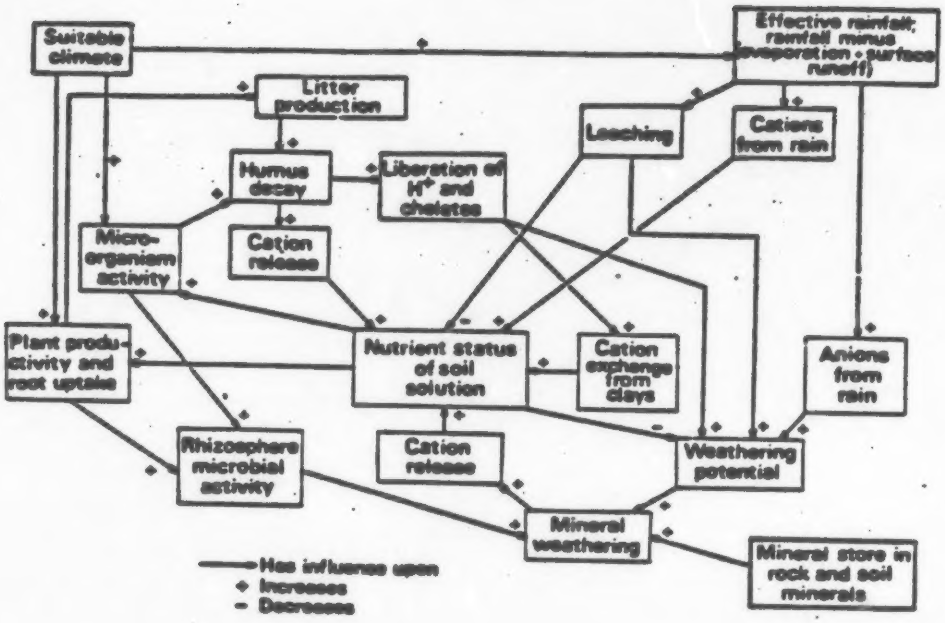

Suitable climate
Effective rainfall; rainfall minus (evaporation + surface runoff)
Litter production
Leaching
Cations from rain
Humus decay
Liberation of H+ and chelates
Micro-organism activity
Cation release
Plant productivity and root uptake
Nutrient status of soil solution
Cation exchange from clays
Anions from rain
Rhizosphere microbial activity
Cation release
Weathering potential
Mineral weathering
Mineral store in rock and soil minerals
Has influence upon
+ Increases
- Decreases

Figure A.4.23. Schematic of computer simulation model. See Table 1 for details. The a.n.c. is the acid neutralizing capacity of soil horizon (source: Booty and Kramer, 1984).

Table A.4.19. Summary of methods to represent hydrological and chemical processes in the Booty and Kramer (1984) model.

Hydrology	Processes
canopy interception	moisture balance between precipitation, evapotranspiration, and canopy storage capacity;
snow accumulation	evenly distributed and measured as equivalents;
snowmelt	temperature and rain induced for forested and open areas;
surface runoff	only considered to be significant over exposed bedrock or over frozen soil during the spring melt;
streamflow	based on the continuity equation for low order streams;
infiltration	all moisture in excess of interception storage is assumed to go directly to infiltration; snowmelt will infiltrate the soil if the ground is not frozen which is determined by the degree-day method;
soil moisture	water balance between storage, interflow, evapotranspiration, and percolation for each soil horizon;
evapotranspiration	empirical formulae using air temperature and relative humidity;
percolation	moisture in excess of field capacity which increases linearly to the saturated hydraulic conductivity of the soil horizon at saturation;
groundwater flow	linear flow based on tohe Darcy equation;
lake	water balance between precipitation, streamwater and groundwater inflows, evaporation, and lake outflows single or multi-layer;
time interval	daily time step;
intput-output	input daily precipitation depth, mean daily temperature, and vapor pressure; output canopy moisture content, soil horizon moisture contents, streamflow groundwater flow, lake and basin outflow volumes;
Chemistry	
canopy modification	determined by the use of attenuation-enrichment coefficients for specific tree species;
snowpack and snowmelt	snowpack water and snowmelt are treated as aqueous carbonate systems; exponential function is used to determine ion enrichment of early snowmelt;
streamfwater	mass balance of conservative ions at a control point (aqueous carbonate system);
soil water	acid neutralization capacity functions determined analytically for each soil horizon; functions incorporate cation exchange and mineral dissolution over specific pH ranges;
lake	aqueous carbonate system modified by biological reactions;

Input: daily precipitation pH and alkalinity.

Output: pH of soil horizon waters, pH of streamwater, pH of groundwater, pH of lakewater.

4.7 CONCLUSIONS

4.7.1 Advantages and Utility of Approaches

The preceding sections discussed various static and dynamic methods for assessing system response. Each method has been used to implicitly or explicitly characterize and categorize a system's historical state or response, its present state, or to predict future responses. Although each method provides useful information for evaluating system response, each method also has inherent assumptions and limitations that must be incorporated in the interpretation and conclusions of results. Historical trends analyses, for example, may indicate a time trend for a particular variable that may be useful in predicting its future state or values. An important assumption, however, is that historical environmental conditions will be repeated or continue in the future. Single factor response time estimates indicate the relative response of the system to the rate of change of an isolated or individual process. These processes, however, are highly interactive and do not operate in isolation. The greatest advantage in having many applicable methods lies in the integration of these results for a holistic perspective of system response.

4.7.2 Integration of Approaches

There is still a great deal of uncertainty associated with our understanding of the processes that influence surface water acidification. Although each of the methods discussed in this chapter has inherent assumptions and limitations, their combined use can provide corroborative support for resulting conclusions. If each of the methods produces similar results, the final conclusions may be derived with greater confidence than from using only a single method. Conversely, if the methods diverge in their results, additional review of the data, assumptions, and other factors is necessary and warranted.

Therefore, it is important to consider the merits of each approach in the context of the others. The integration of statistical analyses, input-output budgets, single factor response time estimates, dynamic systems model simulations, and other approaches can significantly improve our knowledge and understanding of process important in surface water acidification.

4.7.3 Recommendations/Limitations for Further Model Development

The dynamic models discussed in Section 4.6 represent our current hypotheses on the mechanisms and process interactions that control surface water acidification. As working hypotheses, these models need to be tested using field and laboratory data. The models can be tested in three ways. First, where possible, these models should be calibrated on one or two years of data. Simulated water chemistry and actual water chemistry should be compared for successive years of data. Second, these models should be calibrated on one watershed and then used to simulate the water chemistry in a similar watershed, changing only those parameters (e.g., soil depth, watershed area, etc.) and input values (e.g., meteorological inputs, etc.) required to characterize the physical regime of the test watersheds. These two exercises require data that are presently available, albeit limited both in length of record and number of intensively studied watersheds. The third model test should occur on an experimental manipulation of a whole watershed or catchment. This experiment can be used to evaluate not only time variations in water chemistry but also the conceptual basis of the models and rate estimates for various mechanisms.

Mathematical models generally are data limited. Our ability to formulate model equations exceeds the available data to test these models. Experimentation and intensively studied watershed studies are required for model improvement. Because of this lack of data, these models should be viewed as heuristic tools to improve our understanding of surface water acidification. These models have not been verified and should represent working hypotheses. Their predictive uncertainty is unknown. Therefore, they cannot be used to provide precise, accurate estimates of the interactions among acid deposition and surface water chemistry. The models can, however, be used:

1. to test hypotheses concerning acidic deposition and surface water chemistry;
2. and to classify systems with respect to their response time characteristics (i.e., direct response, delayed response, and capacity protected systems).

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